

Volume 10: Fused Five-Membered Heteroarenes with One Heteroatom

	Preface	V
	Table of Contents	IX
	Introduction	
	E. J. Thomas	1
10.1	Product Class 1: Benzo[b]furans	
	C. P. Dell	11
10.2	Product Class 2: Benzo[c]furans	
	P. G. Steel	87
10.3	Product Class 3: Dibenzofurans	
	K. Jones	131
10.4	Product Class 4: Benzo[b]thiophenes	
	C. M. Rayner and M. A. Graham	155
10.5	Product Class 5: Benzo[c]thiophenes	
	T. L. Gilchrist and S. J. Higgins	185
10.6	Product Class 6: Dibenzothiophenes	
	M. D. Andrews	211
10.7	Product Class 7: Benzo[b]selenophenes	
	P. J. Murphy	265
10.8	Product Class 8: Benzo[c]selenophenes	
	P. J. Murphy	301
10.9	Product Class 9: Dibenzoselenophenes	
	P. J. Murphy	307
10.10	Product Class 10: Benzo[b]tellurophenes	
	P. J. Murphy	325
10.11	Product Class 11: Benzo[c]tellurophenes	
	P. J. Murphy	343
10.12	Product Class 12: Dibenzotellurophenes	
	P. J. Murphy	347
10.13	Product Class 13: Indole and Its Derivatives	
	J. A. Joule	361
10.14	Product Class 14: 1<i>H</i>- and 2<i>H</i>-Isoindoles	
	T. J. Donohoe	653
10.15	Product Class 15: Carbazoles	
	P. T. Gallagher	693
10.16	Product Class 16: Indolizines	
	M. Shipman	745

10.17	Product Class 17: Benzo[b]phospholes	
	R. A. Aitken	789
10.18	Product Class 18: Benzo[c]phospholes	
	R. A. Aitken	809
10.19	Product Class 19: Dibenzophospholes	
	R. A. Aitken	817
10.20	Product Class 20: Phosphorus Analogues of Indolizines	
	R. A. Aitken	839
	Keyword Index	843
	Author Index	861
	Abbreviations	911

Table of Contents

Introduction

E. J. Thomas

	Introduction	1
10.1	Product Class 1: Benzo[<i>b</i>]furans C. P. Dell	
10.1	Product Class 1: Benzo[<i>b</i>]furans	11
10.1.1	Synthesis by Ring-Closure Reactions	17
10.1.1.1	By Annulation to an Arene	17
10.1.1.1.1	By Formation of One O—C and One C—C Bond	17
10.1.1.1.1.1	Method 1: From 2-Halophenols and Alkynes	18
10.1.1.1.1.1.1	Variation 1: Using a Copper(I) Acetylide	18
10.1.1.1.1.1.2	Variation 2: Using an Alkyne and Copper(I) Oxide	18
10.1.1.1.1.1.3	Variation 3: Using an Alkyne and Copper Powder	19
10.1.1.1.1.1.4	Variation 4: Using an Alkyne with Palladium(II) and Copper(I) Catalysis in the Presence of an Organic Base	19
10.1.1.1.1.1.5	Variation 5: Using an Alkyne with Palladium(II) and Copper(I) Catalysis in the Presence of an Inorganic Base	21
10.1.1.1.1.1.6	Variation 6: Using an Alkyne with Palladium(II) and Copper(I); Combinatorial Procedure	21
10.1.1.1.1.1.7	Variation 7: Using an Alkyne with Palladium(II)	22
10.1.1.1.1.1.8	Variation 8: By Photochemical Trapping of Zwitterions	23
10.1.1.1.1.2	Method 2: From 1,4-Quinones	23
10.1.1.1.1.3	Method 3: From 2-Hydroxybenzaldehydes and 2-Hydroxyphenyl Ketones	24
10.1.1.1.1.3.1	Variation 1: Using Phenacyl Bromide	25
10.1.1.1.1.3.2	Variation 2: Using Phenacyl Bromide Under Phase-Transfer Conditions	25
10.1.1.1.1.3.3	Variation 3: Using Bromoacetaldehyde	26
10.1.1.1.1.3.4	Variation 4: Using Chloroacetone	26
10.1.1.1.1.3.5	Variation 5: Using Ethyl Bromoacetate	27
10.1.1.1.1.3.6	Variation 6: Using Ethyl Chloroacetoacetate	28
10.1.1.1.1.3.7	Variation 7: Using Bromonitromethane	28
10.1.1.1.1.3.8	Variation 8: Using Diethyl α -Bromomalonate	29
10.1.1.1.1.3.9	Variation 9: Using Benzyl Halides	29
10.1.1.1.1.4	Method 4: From Methyl 2-Hydroxybenzoates	30
10.1.1.1.1.5	Method 5: From Phenols and α -Haloacyl Halides	30
10.1.1.1.1.6	Method 6: By Intramolecular Wittig Reactions	31
10.1.1.1.1.7	Method 7: From <i>O</i> -Arylketoximes	31
10.1.1.1.1.8	Method 8: By Claisen Rearrangement of Phenyl Propargyl Ethers and Related Species	32

10.1.1.1.1.8.1	Variation 1:	By Claisen Rearrangement of Phenyl Propargyl Ethers	32
10.1.1.1.1.8.2	Variation 2:	By Claisen Rearrangement of Phenyl Propargyl Ethers Using Cesium Fluoride	33
10.1.1.1.1.8.3	Variation 3:	By Claisen Rearrangement of Aryl 2-Chloroprop-2-enyl Ethers	34
10.1.1.1.2		By Formation of Two C—C Bonds	35
10.1.1.1.2.1	Method 1:	By One-Pot, Acid-Catalyzed Cyclization of α -Aryloxy Ketones	35
10.1.1.1.3		By Formation of One O—C Bond	36
10.1.1.1.3.1	Method 1:	From 2-Ethynylphenols and Their Derivatives	36
10.1.1.1.3.1.1	Variation 1:	From a 2-Ethynylphenol with Palladium Catalysis	37
10.1.1.1.3.1.2	Variation 2:	From a 2-Alkynylphenol with Palladium Catalysis: Introduction of Acyl Functionality	37
10.1.1.1.3.1.3	Variation 3:	From a 2-[(Trimethylsilyl)ethynyl]phenyl Acetate with Palladium Catalysis	38
10.1.1.1.3.1.4	Variation 4:	From 2-Alkynylphenols and Allyl Carbonates with Palladium Catalysis	39
10.1.1.1.3.1.5	Variation 5:	From 2-(Triisopropylsiloxy)phenylalkynes	40
10.1.1.1.3.1.6	Variation 6:	From 4-(2-Hydroxyaryl)-1,2,3-thiadiazoles	41
10.1.1.1.3.1.7	Variation 7:	From Dealkylation of 2-Methoxyphenylalkynes	41
10.1.1.1.3.1.8	Variation 8:	From Flash-Vacuum Pyrolysis of (2-Methoxybenzoyl)alkylidetriphenylphosphoranes	42
10.1.1.1.3.1.9	Variation 9:	Treatment of 2-Methoxyphenylalkynes with Mercury(II) Acetate	42
10.1.1.1.3.2	Method 2:	From 2-Alkenylphenols Using Palladium Reagents	44
10.1.1.1.3.2.1	Variation 1:	From a 2-Allylphenol with Bis(benzonitrile)dichloropalladium(II)	44
10.1.1.1.3.2.2	Variation 2:	From a 2-Hydroxystyrene	44
10.1.1.1.3.3	Method 3:	Benzofuran-3(2 <i>H</i>)-ones and Benzofuran-3-ols from α -Halo-2-hydroxyacetophenones	45
10.1.1.1.3.3.1	Variation 1:	Two Steps Using Chloroacetyl Chloride	45
10.1.1.1.3.3.2	Variation 2:	Two Steps Using Chloroacetonitrile	46
10.1.1.1.3.3.3	Variation 3:	Via Bromination of a 2-Hydroxyacetophenone	46
10.1.1.1.3.4	Method 4:	From Enol Radical Cations	47
10.1.1.1.4		By Formation of One C—C Bond	48
10.1.1.1.4.1	Method 1:	By [2 + 2] Cycloadditions with Ketenes	48
10.1.1.1.4.1.1	Variation 1:	By [2 + 2] Cycloadditions with Ketenes	49
10.1.1.1.4.1.2	Variation 2:	By [2 + 2] Cycloadditions with Ketenes: Perkin Conditions	49
10.1.1.1.4.2	Method 2:	By Cyclization of <i>O</i> -Allyl-2-halophenols and Related Species	50
10.1.1.1.4.2.1	Variation 1:	From an <i>O</i> -Allyl-2-halophenol with Palladium Catalysis	50
10.1.1.1.4.2.2	Variation 2:	From an <i>O</i> -Allyl-2-mercuriophenol with Stoichiometric Palladium	51
10.1.1.1.4.2.3	Variation 3:	From <i>O</i> -Propargyl- and <i>O</i> -Allenyl-2-iodophenols	51
10.1.1.1.4.2.4	Variation 4:	From a 3-(2-Haloprop-2-enyloxy)phenol with Palladium	52
10.1.1.1.4.3	Method 3:	By Acid-Catalyzed Cyclization of α -Aryloxy Carbonyl Compounds and Their Derivatives	53

10.1.1.1.4.3.1	Variation 1:	Cyclization of α -Aryloxy Ketones	53
10.1.1.1.4.3.2	Variation 2:	Cyclization of α -Aryloxycarboxylic Acids	55
10.1.1.1.4.3.3	Variation 3:	Cyclization of α -Aryloxycarboxamides	56
10.1.1.1.4.3.4	Variation 4:	Cyclization of Protected α -Aryloxyaldehydes	56
10.1.1.1.4.4	Method 4:	By Cyclization of O-Substituted 2-Hydroxybenzaldehydes and Related Species	57
10.1.1.1.4.5	Method 5:	By Dieckmann Cyclization of (2-Alkoxy-carbonylphenoxy)acetic Acids and Esters	58
10.1.1.1.4.6	Method 6:	By Cyclization of 2-(Benzyloxy)benzaldehydes and Related Species	59
10.1.1.2	By Annulation to the Heterocyclic Ring		60
10.1.1.2.1	By Formation of Three and Two C—C Bonds		60
10.1.1.2.1.1	Method 1:	From 2-Vinylfurans	60
10.1.1.2.1.1.1	Variation 1:	From 2-Vinylfurans (Intermolecular Cycloaddition)	61
10.1.1.2.1.1.2	Variation 2:	From 2-Vinylfurans (Intramolecular Cycloaddition)	61
10.1.1.2.1.2	Method 2:	From 3-Vinylfurans (Intermolecular Cycloaddition)	62
10.1.1.2.1.3	Method 3:	From Furan Analogues of 1,2-Quinodimethane	63
10.1.1.2.1.4	Method 4:	By Conjugate Addition—Cyclization	64
10.1.1.2.1.5	Method 5:	From Cyclobutenones	64
10.1.1.2.1.6	Method 6:	From Benzannulation of Furyl Chromium Carbene Complexes	65
10.1.1.2.1.7	Method 7:	Using 2-(Benzotriazol-1-ylmethyl)furans	65
10.1.1.2.1.8	Method 8:	By Carbonylation of Vinylfurans	66
10.1.1.2.2	By Formation of One C—C Bond		67
10.1.1.2.2.1	Method 1:	By Stobbe and Related Condensations	67
10.1.1.2.2.2	Method 2:	From Electrocyclic Reactions of 2,3-Disubstituted Furans	68
10.1.2	Synthesis by Ring Transformation		68
10.1.2.1	Method 1:	By Ring Enlargement	68
10.1.2.2	Method 2:	By Formal Exchange of Ring Members with Retention of Ring Size	69
10.1.2.3	Method 3:	By Ring Contraction	70
10.1.2.3.1	Variation 1:	By Ring Contraction of 1-Benzopyrylium Salts	70
10.1.2.3.2	Variation 2:	By Ring Contraction of 4-(Halomethyl)coumarins	70
10.1.3	Aromatization		71
10.1.4	Synthesis by Substituent Modification		71
10.1.4.1	Addition Reactions		71
10.1.4.2	Substitution of Existing Substituents		71
10.1.4.2.1	Of Hydrogen		71
10.1.4.2.1.1	Method 1:	Metalation	72
10.1.4.2.1.2	Method 2:	Acylation	72
10.1.4.2.1.3	Method 3:	Alkylation, Alkenylation, and Arylation	73
10.1.4.2.1.4	Method 4:	Halogenation	73
10.1.4.2.1.5	Method 5:	Nitration	74

10.1.4.2.2	Of Carbon Functionalities	75
10.1.4.3	Modification of Substituents	75
10.1.4.4	Rearrangement of Substituents	75
10.2	Product Class 2: Benzo[c]furans	
	P. G. Steel	
<hr/>		
10.2	Product Class 2: Benzo[c]furans	87
10.2.1	Synthesis by Ring-Closure Reactions	88
10.2.1.1	By Formation of both Benzene and Furan Rings	88
10.2.1.1.1	Method 1: By Cyclization–Dehydration of 1,2-Diaroylcyclohexenes	88
10.2.1.1.1.1	Variation 1: From 3-Substituted 1,2-Diaroylcyclohexenes	88
10.2.1.1.1.2	Variation 2: From 1,2-Diaroylcyclohexadienes	89
10.2.1.2	By Annulation to an Arene	90
10.2.1.2.1	By Formation of One Heteroatom—Carbon Bond	90
10.2.1.2.1.1	Method 1: From 1,2-Diacylbenzenes	90
10.2.1.2.1.1.1	Variation 1: Reduction with Hydride Reducing Agents	90
10.2.1.2.1.1.2	Variation 2: Reduction with Dissolving Metals	91
10.2.1.2.1.1.3	Variation 3: Nucleophilic Addition to 2-Acylbenzaldehydes	91
10.2.1.2.2	Method 2: From 2-Acylbenzyl Alcohols	92
10.2.1.2.2.1	Variation 1: Via 2-Acylbenzyl Alcohols from Monoacetals of Phthalaldehyde	93
10.2.1.2.2.2	Variation 2: Via 2-Acylbenzyl Alcohols from <i>o</i> -Metalation Strategies	94
10.2.1.2.2.3	Variation 3: Via 2-Acylbenzyl Alcohols from the Anionic Fries Rearrangement of 2-Iodobenzylic Esters	95
10.2.1.2.3	Method 3: Via Intramolecular Trapping of a Benzylic Carbene	96
10.2.1.2.3.1	Variation 1: Via Carbenes from Metal-Catalyzed Diazoalkane Decomposition	97
10.2.1.2.3.2	Variation 2: Via Carbenes from 1,1-Elimination of α -Halosilanes	98
10.2.1.2.3.3	Variation 3: Via Carbenes from Decomposition of Tosylhydrazones	99
10.2.1.2.4	Method 4: Via Displacement of Benzylic Halogen	99
10.2.1.2.4.1	Variation 1: From 2-Alkylbenzophenones	99
10.2.1.2.4.2	Variation 2: From 2-Alkylbenzamides via Imidate Salts	100
10.2.1.2.5	Method 5: From 2-Formylstyrenes	101
10.2.1.2.6	Method 6: 1-Sulfanylbenzo[c]furans via Pummerer Reaction	102
10.2.1.2.6.1	Variation 1: 3-Aryl(alkyl)-1-sulfanylbenzo[c]furans via Thermal Pummerer Reaction	102
10.2.1.2.6.2	Variation 2: Sulfanylbenzo[c]furans via Low-Temperature Pummerer Reaction	103
10.2.1.2.6.3	Variation 3: 3-Amino-1-Sulfanylbenzo[c]furans via Pummerer Reaction of <i>o</i> -Amido Sulfoxides	103
10.2.1.3	By Annulation to a Furan	104
10.2.1.3.1	Method 1: Via Condensations of 3,4-Diformylfurans	105

10.2.2	Synthesis by Ring Transformation	105
10.2.3	Aromatization	106
10.2.3.1	Method 1: Nucleophilic Additions to Phthalides	106
10.2.3.2	Method 2: Via 1,4-Elimination from 1-Alkoxyphthalans	106
10.2.3.2.1	Variation 1: Thermal Generation of Benzo[c]furan from Alkoxyphthalans	107
10.2.3.2.2	Variation 2: Via Acid-Catalyzed 1,4-Elimination of Alkoxyphthalans	108
10.2.3.2.3	Variation 3: Via Amide Base Promoted 1,4-Elimination of Alkoxyphthalans	109
10.2.3.2.4	Variation 4: Via Catalytic Amide Base Promoted 1,4-Elimination of Alkoxyphthalans	110
10.2.3.2.5	Variation 5: Via 1,4-Elimination of Alkoxyphthalans with in situ Silylation	111
10.2.3.3	Method 3: Via Elimination from Phthalan Hemiaminals	112
10.2.3.4	Method 4: Via Isomerization (Aromatization) of Alkylidenephthalans ...	113
10.2.3.4.1	Variation 1: From Arylidenephthalans	113
10.2.3.4.2	Variation 2: From Phthalides via Alkylidenephthalans	114
10.2.3.5	Method 5: From Phthalide Anions (Aromatization via Deprotonation) ...	115
10.2.3.5.1	Variation 1: From Phthalide Anions	116
10.2.3.5.2	Variation 2: From Stabilized Phthalide Anions	117
10.2.3.5.3	Variation 3: Siloxybenzo[c]furans from Phthalide Anions	117
10.2.3.6	Method 6: Via Retro-Diels–Alder Reactions	118
10.2.3.6.1	Variation 1: Thermal Decomposition of Pyrone Adducts	119
10.2.3.6.2	Variation 2: Via Reaction of 1,4-Epoxy-1,4-dihydronaphthalenes with 3,6-Di-2'-pyridyl-1,2,4,5-tetrazine	119
10.2.3.6.3	Variation 3: Flash-Vacuum Pyrolysis of 1,4-Epoxy-1,2,3,4-tetrahydronaphthalenes	121
10.2.3.6.4	Variation 4: Via Extrusion of Nitriles	121
10.2.3.7	Method 7: Via Aromatization of the Arene Ring	122
10.2.3.7.1	Variation 1: Via Dehydrobromination of Bromocyclohexenes	122
10.2.3.7.2	Variation 2: Via Dehydration of Furanocyclohexenols	123
10.2.4	Synthesis by Substituent Modification	125
10.2.4.1	Substitution of Existing Substituents	125
10.2.4.1.1	Of Hydrogen	125
10.2.4.1.1.1	Method 1: Alkylation of Lithiobenzo[c]furans	125
10.2.4.1.1.2	Method 2: Substituted Benzo[c]furans via Ring Opening of Cycloadducts	127
10.3	Product Class 3: Dibenzofurans K. Jones	
10.3	Product Class 3: Dibenzofurans	131
10.3.1	Synthesis by Ring-Closure Reactions	133
10.3.1.1	By Formation of the Furan Ring	133
10.3.1.1.1	By Formation of Two O—C Bonds	134
10.3.1.1.1.1	Method 1: From 2,2'-Dihalobiphenyls	134

10.3.1.1.2	By Formation of One O—C and One C—C Bond	135
10.3.1.1.2.1	Method 1: From Cyclohexa-1,3-diones and 2-Halocyclohexanones (Feist–Benary Synthesis)	135
10.3.1.1.2.2	Method 2: From Quinones and Cyclohexanone Enamines	136
10.3.1.1.2.3	Method 3: From Phenolate Ions and 2-Halocyclohexanones (Ebel’s Method)	136
10.3.1.1.2.4	Method 4: From Phenols via Oxidative Coupling	137
10.3.1.1.3	By Formation of One O—C Bond	138
10.3.1.1.3.1	Method 1: From 2,2’-Dihydroxybiphenyls	138
10.3.1.1.3.2	Method 2: From 2-Halo-2’-hydroxybiphenyls	139
10.3.1.1.3.3	Method 3: From 2-Amino-2’-methoxybiphenyls	139
10.3.1.1.4	By Formation of One C—C Bond	140
10.3.1.1.4.1	Method 1: From 2,2’-Diiododiphenyl Ethers	140
10.3.1.1.4.2	Method 2: From 2-Aminodiphenyl Ethers	141
10.3.1.1.4.2.1	Variation 1: From 2-Phenoxybenzenediazonium Salts under Acidic Conditions	141
10.3.1.1.4.2.2	Variation 2: From 2-Phenoxybenzenediazonium Salts on Treatment with Electron Donors	142
10.3.1.1.4.3	Method 3: Cyclization of Diphenyl Ethers	142
10.3.1.1.4.3.1	Variation 1: From Diphenyl Ethers Using Stoichiometric Palladium(II) Acetate	143
10.3.1.1.4.3.2	Variation 2: From Diphenyl Ethers Using Catalytic Palladium(II) Acetate	144
10.3.1.1.4.3.3	Variation 3: From Diphenyl Ethers by Photochemical Cyclization	145
10.3.1.2	By Annulation to Benzo[<i>b</i>]furans	146
10.3.1.2.1	By Formation of Two C—C Bonds	146
10.3.1.2.1.1	Method 1: From 2-Methylbenzo[<i>b</i>]furan-3-carbaldehydes	146
10.3.1.2.1.2	Method 2: From 2-Vinylbenzo[<i>b</i>]furans	147
10.3.1.2.2	By Formation of One C—C Bond	147
10.3.1.2.2.1	Method 1: Via Intramolecular Claisen Condensation	148
10.3.1.2.2.2	Method 2: Via Intramolecular Friedel–Crafts Acylation	148
10.3.2	Synthesis by Ring Transformation	149
10.3.2.1	Method 1: From Quinone–Cyclohexadiene Cycloaddition Adducts	149
10.3.2.2	Method 2: From Spirobenzo[<i>b</i>]furanones	150
10.3.3	Additional Methods	150

10.4	Product Class 4: Benzo[<i>b</i>]thiophenes C. M. Rayner and M. A. Graham	
10.4	Product Class 4: Benzo[<i>b</i>]thiophenes	155
10.4.1	Synthesis by Ring-Closure Reactions	156
10.4.1.1	By Annulation to an Arene	157
10.4.1.1.1	By Formation of Two S—C Bonds and One C—C Bond	157
10.4.1.1.1.1	Method 1: Zirconium-Mediated Coupling of Aryllithium Reagents with Alkynes and Sulfur Dichloride	157
10.4.1.1.2	By Formation of Two S—C Bonds	158
10.4.1.1.2.1	Method 1: Condensation of Styrenes with Sulfur	158
10.4.1.1.3	By Formation of One S—C and One C—C Bond	158
10.4.1.1.3.1	Method 1: From Phosphonium Salts	158
10.4.1.1.3.2	Method 2: Perkin Condensation	159
10.4.1.1.4	By Formation of Two C—C Bonds	160
10.4.1.1.4.1	Method 1: By Lithiation of Thioanisole	160
10.4.1.1.5	By Formation of One S—C Bond	161
10.4.1.1.5.1	Method 1: Oxidative Cyclization of <i>o</i> -Sulfanylcinnamic Acids with Subsequent Decarboxylation	161
10.4.1.1.5.2	Method 2: Electrophilic Cyclization of 2-Sulfanylcinnamic Acids	162
10.4.1.1.5.3	Method 3: Cyclization of (<i>E</i>)- β -Chlorovinylsulfenamides to 2-Substituted 3-Chlorobenzo[<i>b</i>]thiophenes	163
10.4.1.1.5.4	Method 4: Cyclization of [2-(Benzylsulfanyl)phenyl]acetonitrile	163
10.4.1.1.6	By Formation of One C—C Bond	164
10.4.1.1.6.1	Method 1: Cyclization of 2-(Phenylsulfanyl)acetaldehyde Dialkyl Acetals and Related Compounds	164
10.4.1.1.6.2	Method 2: Dieckmann Condensation	166
10.4.1.1.6.3	Method 3: Intramolecular Heck Cyclization	166
10.4.1.2	By Annulation to the Heterocyclic Ring	167
10.4.1.2.1	By Formation of Two C—C Bonds	167
10.4.1.2.1.1	Method 1: By the Diels–Alder Reaction	167
10.4.1.2.1.2	Method 2: By Michael Addition of a Thienylmethyl Anion	167
10.4.1.2.1.3	Method 3: By Metal-Mediated Cross Coupling of 2,3-Disubstituted 4-Chlorocyclobut-2-enones	168
10.4.1.2.1.4	Method 4: Cyclocarbonylation of 3-Thienylallyl Acetates	169
10.4.1.2.2	By Formation of One C—C Bond	169
10.4.1.2.2.1	Method 1: Photolysis of (Naphthylvinyl)thiophenes to Phenanthro[<i>b</i>]thiophenes	169
10.4.2	Synthesis by Substituent Modification	170
10.4.2.1	Substitution of Existing Substituents	170

10.4.2.1.1	Of Hydrogen	170
10.4.2.1.1.1	Method 1: Metalation	170
10.4.2.1.1.2	Method 2: C-Acylation	171
10.4.2.1.1.3	Method 3: C-Alkylation	172
10.4.2.1.1.4	Method 4: Cerium(IV)-Mediated Addition of a Malonyl Radical to Benzo[<i>b</i>]thiophene	173
10.4.2.1.1.5	Method 5: C-Halogenation	173
10.4.2.1.2	Of Metals	174
10.4.2.1.2.1	Method 1: Reactions Involving Organopalladium Derivatives	174
10.4.2.1.2.2	Method 2: Reactions Involving Organolithium Intermediates	175
10.4.2.1.3	Of Carbon Functionalities	177
10.4.2.1.3.1	Method 1: Curtius Rearrangement of Carboxylic Acids	177
10.4.2.1.4	Of Heteroatoms	177
10.4.2.1.4.1	Method 1: Metal–Halogen Exchange	177
10.4.2.1.4.2	Method 2: Palladium-Mediated Coupling of Halobenzo[<i>b</i>]thiophenes	178
10.4.2.1.4.3	Method 3: Reactions of Diazonium Salts	179
10.4.2.2	Modification of Substituents	181
10.4.2.2.1	Method 1: Reduction of Nitro Derivatives	181
10.5	Product Class 5: Benzo[<i>c</i>]thiophenes	
	T. L. Gilchrist and S. J. Higgins	
10.5	Product Class 5: Benzo[<i>c</i>]thiophenes	185
10.5.1	Synthesis by Ring-Closure Reactions	187
10.5.1.1	By Annulation to an Arene	187
10.5.1.1.1	By Formation of Two S–C Bonds	187
10.5.1.1.1.1	Method 1: From 1,2-Diacylbenzenes and Phosphorus Pentasulfide	188
10.5.1.1.1.1.1	Variation 1: Use of Lawesson’s Reagent	188
10.5.1.1.1.1.2	Variation 2: Reaction of 1,2-Dibenzylbenzenes with Sulfur	189
10.5.1.1.2	By Formation of One S–C and One C–C Bond	190
10.5.1.1.2.1	Method 1: Reaction of Thiobenzophenones with Bis(arenesulfonyl)diazomethanes	190
10.5.1.1.3	By Formation of Two C–C Bonds	190
10.5.1.1.3.1	Method 1: Use of the Hinsberg Thiophene Synthesis for <i>c</i> -Fused Thiophenes	191
10.5.1.1.4	By Formation of One C–C Bond	192
10.5.1.1.4.1	Method 1: Intramolecular Nucleophilic Substitution of Fluoroarenes	192
10.5.1.2	By Annulation to a Thiophene Ring	192
10.5.1.2.1	Method 1: Addition of (3-Thienyl)methyl 4-Tolyl Sulfones to Conjugated Alkenes	194

10.5.2	Synthesis by Ring Transformation	195
10.5.2.1	Method 1: From Isobenzofurans	195
10.5.2.2	Method 2: Via Cyclic Rhodium Complexes Derived from Bis(phenylethynyl)arenes	196
10.5.2.3	Method 3: Ring Contraction of 1,4-Dihydrobenzodithiins	197
10.5.2.4	Method 4: Ring Contraction of Benzothiins	197
10.5.3	Aromatization	199
10.5.3.1	Method 1: From 1,3-Dihydrobenzo[c]thiophene 2-Oxides	201
10.5.3.1.1	Variation 1: Aromatization of 2-Methoxy-1,3-dihydro- benzo[c]thiophenylum Trifluoromethanesulfonates	202
10.5.3.2	Method 2: Dechlorination of 1,1,3,3-Tetrachloro-1,3-dihydro- benzo[c]thiophene	203
10.5.4	Synthesis by Substituent Modification	203
10.5.4.1	Method 1: Displacement Reactions Based on 1,3-Dichlorobenzo[c]thiophene	204
10.5.5	Synthesis of Poly(benzo[c]thiophenes)	205
10.6	Product Class 6: Dibenzothiophenes M. D. Andrews	
10.6	Product Class 6: Dibenzothiophenes	211
10.6.1	Synthesis by Ring-Closure Reactions	213
10.6.1.1	By Annulation to an Arene	214
10.6.1.1.1	By Formation of Two S—C Bonds	214
10.6.1.1.1.1	Method 1: From Biphenyl Using Sulfur and Aluminum Trichloride	214
10.6.1.1.1.2	Method 2: From Biaryls Using Hydrogen Sulfide and a Catalyst	215
10.6.1.1.1.3	Method 3: From Biaryl-2,2'-diols and Phosphorus Pentasulfide	215
10.6.1.1.1.4	Method 4: From Biaryls and Sulfur Dichloride	216
10.6.1.1.1.5	Method 5: From Biaryls and Oleum or Chlorosulfonic Acid	217
10.6.1.1.1.6	Method 6: From 3-Arylcyclohex-2-enones	218
10.6.1.1.2	By Formation of One S—C and One C—C Bond	219
10.6.1.1.2.1	Method 1: Via Cyclization of α -Arylsulfonyl Ketones	219
10.6.1.1.2.1.1	Variation 1: The Tilak Annulation	219
10.6.1.1.2.1.2	Variation 2: From an Epoxycyclohexanone	222
10.6.1.1.2.2	Method 2: From Tetrafluorobenzynes	223
10.6.1.1.3	By Formation of One S—C Bond	223
10.6.1.1.3.1	Method 1: From Arenesulfonyl or Arenesulfinyl Chlorides	223
10.6.1.1.3.2	Method 2: By Oxidation of 2-[(Trifluoromethyl)sulfonyl]biphenyls	224
10.6.1.1.4	By Formation of One C—C Bond	225
10.6.1.1.4.1	Method 1: The Pschorr Cyclization	225
10.6.1.1.4.2	Method 2: By Treatment of Diaryl Sulfoxides with Base	227

10.6.1.1.4.3	Method 3: Photocyclization of Diaryl Sulfides	227
10.6.1.1.4.4	Method 4: Vacuum Pyrolysis of Aryl Radical Precursors	228
10.6.1.1.5	Additional Methods	229
10.6.1.2	By Annulation to the Heterocyclic Ring	229
10.6.1.2.1	By Formation of Two C—C Bonds	229
10.6.1.2.1.1	Method 1: By Reaction of Dichloromethyl Ethers with Allylbenzo[<i>b</i>]thiophenes	229
10.6.1.2.1.2	Method 2: Diels–Alder Reactions of Benzo[<i>b</i>]thiophene 1,1-Dioxides	231
10.6.1.2.1.3	Method 3: Diels–Alder Reactions of Vinylbenzo[<i>b</i>]thiophenes	232
10.6.1.2.1.4	Method 4: Via Coupling of Cyclobutenones with Organostannanes	233
10.6.1.2.1.5	Method 5: Via Benzothieno[2,3- <i>c</i>]pyrylium Salts	234
10.6.1.2.1.6	Method 6: From 2-Benzoyl-3-chlorobenzo[<i>b</i>]thiophene 1,1-Dioxide	235
10.6.1.2.1.7	Method 7: By Double Friedel–Crafts Alkylation Reactions	236
10.6.1.2.2	By Formation of One C—C Bond	237
10.6.1.2.2.1	Method 1: Photocyclization of 1,2-Diarylalkenes	237
10.6.1.2.2.2	Method 2: By Cyclization of Aromatic Aldehydes or Ketones (The Bradsher Reaction)	239
10.6.1.2.2.3	Method 3: Intramolecular Friedel–Crafts Acylation Reactions	240
10.6.1.2.2.4	Method 4: By Pyrolysis of Aroylbenzo[<i>b</i>]thiophenes (The Elbs Reaction)	241
10.6.1.2.2.5	Method 5: By Thermolysis of (Arylhydroxymethyl)thiophenes	242
10.6.1.2.3	Additional Methods	243
10.6.2	Synthesis by Ring Transformation	243
10.6.2.1	Method 1: Diels–Alder Reactions of Benzothienopyranones	243
10.6.2.2	Method 2: Reduction of Dibenzo[<i>c,e</i>]dithiins	244
10.6.2.3	Method 3: Reaction of Thianthrene 5-Oxides with Organolithiums	244
10.6.2.4	Additional Methods	245
10.6.3	Aromatization	246
10.6.3.1	Method 1: By Dehydrogenation	246
10.6.3.1.1	Variation 1: Palladium on Carbon at High Temperature	246
10.6.3.1.2	Variation 2: Heating with Selenium or Sulfur	246
10.6.3.1.3	Variation 3: Oxidation with Quinone	247
10.6.3.1.4	Variation 4: Halogenation/Dehydrohalogenation	247
10.6.3.2	Method 2: By Elimination	248
10.6.4	Synthesis by Substituent Modification	248
10.6.4.1	Addition Reactions	248
10.6.4.1.1	Method 1: S-Alkylation	248
10.6.4.1.2	Method 2: S-Oxidation	249
10.6.4.1.2.1	Variation 1: Formation of Dibenzothiophene 5,5-Dioxides	249
10.6.4.1.2.2	Variation 2: Formation of Dibenzothiophene 5-Oxides	250
10.6.4.2	Substitution of Existing Substituents	250
10.6.4.2.1	Of Hydrogen	250

10.6.4.2.1.1	Method 1:	Via Metalation	250
10.6.4.2.1.2	Method 2:	Friedel–Crafts Acylation	252
10.6.4.2.1.3	Method 3:	Halogenation	253
10.6.4.2.1.4	Method 4:	Nitration	253
10.6.4.2.2		Of Metals	254
10.6.4.2.3		Of Carbon	255
10.6.4.2.3.1	Method 1:	Decarboxylation	255
10.6.4.2.4		Of Heteroatoms	255
10.6.4.2.4.1	Method 1:	Reduction of Dibenzothiophene 5-Oxides and 5,5-Dioxides	255
10.6.4.2.4.2	Method 2:	Substitution of Halogens	256
10.6.4.2.4.3	Method 3:	Substitution of Nitrogen	257
10.6.4.3		Rearrangement of Substituents	258
10.6.4.4		Modification of Substituents	258
10.7	Product Class 7: Benzo[b]selenophenes		
	P. J. Murphy		
<hr/>			
10.7	Product Class 7: Benzo[b]selenophenes		265
10.7.1	Synthesis by Ring-Closure Reactions		265
10.7.1.1	By Annulation to an Arene		265
10.7.1.1.1	By Formation of Two Se—C Bonds		265
10.7.1.1.1.1	Method 1:	From 1-Arylalk-1-yne and Selenium Tetrahalides	266
10.7.1.1.1.2	Method 2:	From 1-Arylalk-1-yne and Diselenium Dichloride	267
10.7.1.1.1.3	Method 3:	From 1-Arylalk-1-yne, Selenium Dioxide, and Hydrogen Halides	267
10.7.1.1.1.4	Method 4:	From 1,5-Diphenylpenta-1,4-dien-3-one and Selenium Tetrabromide	268
10.7.1.1.1.5	Method 5:	From 1,1-Diarylalkenes and Selenium Oxychloride	269
10.7.1.1.1.6	Method 6:	From 1-(2-Chlorophenyl)ethanone and Lithium Diselenide	269
10.7.1.1.1.7	Method 7:	From Cumulenes and Selenium	270
10.7.1.1.1.8	Method 8:	From Metalated Intermediates	270
10.7.1.1.1.8.1	Variation 1:	From 1-Arylalk-1-yne	270
10.7.1.1.1.8.2	Variation 2:	From 1-(2-Bromophenyl)alk-1-yne	271
10.7.1.1.1.8.3	Variation 3:	From 1-Bromo-2-phenyl- or 1-Bromo- 2-(2-bromophenyl)-1-(trimethylsilyl)ethene	271
10.7.1.1.2	By Formation of One Se—C and One C—C Bond		272
10.7.1.1.2.1	Method 1:	From Diphenyl Diselenide and Dimethyl Acetylenedicarboxylate	272
10.7.1.1.2.2	Method 2:	From Diazodiphenylmethane and Benzoyl Isoselenocyanate	272
10.7.1.1.3	By Formation of One Se—C Bond		273
10.7.1.1.3.1	Method 1:	By Free-Radical Homolytic Substitution at Selenium	273

10.7.1.1.3.2	Method 2:	By Electrophilic Substitution of Styrenes	273
10.7.1.1.3.3	Method 3:	By Cyclodehydration of Ketones	275
10.7.1.1.3.4	Method 4:	Benzo[<i>b</i>]selenophen-2(3 <i>H</i>)-one by Selenolactonization	276
10.7.1.1.3.5	Method 5:	Benzo[<i>b</i>]selenophen-3(2 <i>H</i>)-ones from 2-Acetylareneselenenyl Bromides	276
10.7.1.1.3.6	Method 6:	Benzo[<i>b</i>]selenophen-3(2 <i>H</i>)-one from 1-[2-(Butylselanyl)phenyl]-2-diazoethan-1-one	277
10.7.1.1.4		By Formation of One C—C Bond	278
10.7.1.1.4.1	Method 1:	From Intramolecular Condensations with Aldehydes and Ketones	278
10.7.1.1.4.2	Method 2:	From Intramolecular Condensations of Dicarboxylic Acids	280
10.7.1.1.4.3	Method 3:	From Dieckmann Cyclizations	281
10.7.1.1.4.4	Method 4:	From Cyclization of 2-(Benzylselanyl)arenecarboxanilides	281
10.7.1.1.4.5	Method 5:	Miscellaneous Preparations	282
10.7.1.2		By Annulation to the Heterocyclic Ring	282
10.7.1.2.1	Method 1:	Acylation of Acetylselephenes	282
10.7.2		Synthesis by Ring Transformation	284
10.7.2.1	Method 1:	By Oxidative Ring Contraction	284
10.7.3		Aromatization	285
10.7.3.1	Method 1:	By Dehydrogenation	285
10.7.4		Synthesis by Substituent Modification	285
10.7.4.1		Addition Reactions	285
10.7.4.1.1	Method 1:	Oxidation at Selenium	285
10.7.4.2		Substitution of Existing Substituents	286
10.7.4.2.1		Of Hydrogen	286
10.7.4.2.1.1	Method 1:	Metalation	286
10.7.4.2.1.1.1	Variation 1:	Lithiation	286
10.7.4.2.1.1.2	Variation 2:	Mercuration	286
10.7.4.2.1.2	Method 2:	Friedel–Crafts and Related Reactions	287
10.7.4.2.1.2.1	Variation 1:	Intermolecular Acylation	287
10.7.4.2.1.2.2	Variation 2:	Intramolecular Acylation	288
10.7.4.2.1.2.3	Variation 3:	Arylations and Alkylations	288
10.7.4.2.1.3	Method 3:	Halogenation and Nitration	289
10.7.4.2.2		Of Metals	290
10.7.4.2.2.1	Method 1:	Substitution of Lithium	290
10.7.4.2.2.2	Method 2:	Miscellaneous Substitution of Metals	291
10.7.4.2.3		Of Carbon Functionalities	291
10.7.4.2.3.1	Method 1:	Decarboxylation	291
10.7.4.2.4		Of Heteroatoms	292
10.7.4.2.4.1	Method 1:	Reduction of Benzo[<i>b</i>]selenophen-3(2 <i>H</i>)-ones	292

10.7.4.2.4.2	Method 2:	Reaction of Benzo[<i>b</i>]selenophen-3(2 <i>H</i>)-ones with Carbon Nucleophiles	293
10.7.4.2.4.2.1	Variation 1:	With Grignard Reagents	293
10.7.4.2.4.2.2	Variation 2:	With Wittig Reagents	294
10.7.4.2.4.3	Method 3:	Reaction of Benzo[<i>b</i>]selenophen-3(2 <i>H</i>)-one with Secondary Amines	294
10.7.4.2.4.4	Method 4:	Transmetalation of Halogenated Benzo[<i>b</i>]selenophenes	295
10.7.4.2.4.5	Method 5:	Dehalogenation of Halogenated Benzo[<i>b</i>]selenophenes	295
10.7.4.2.4.6	Method 6:	Nucleophilic Substitution of Halogenated Benzo[<i>b</i>]selenophenes	296
10.7.4.3	Modification of Substituents		296
10.7.4.4	Miscellaneous Reactions		296
10.8	Product Class 8: Benzo[<i>c</i>]selenophenes		
	P. J. Murphy		
10.8	Product Class 8: Benzo[<i>c</i>]selenophenes		
10.8.1	Synthesis by Ring-Closure Reactions		301
10.8.1.1	By Annulation to an Arene		301
10.8.1.1.1	By Formation of Two Se—C Bonds		301
10.8.1.1.1.1	Method 1:	From 2-(Bromomethyl)benzoyl Chloride	301
10.8.1.1.2	By Formation of One Se—C Bond		302
10.8.1.1.2.1	Method 1:	From 2-(Selanyl)methyl)benzoic Acid	302
10.8.2	Synthesis by Ring Transformation		302
10.8.2.1	Method 1:	From Rhodacycles	302
10.8.3	Aromatization		303
10.8.3.1	Method 1:	By Elimination	303
10.8.3.2	Method 2:	By Dehydrogenation	303
10.8.4	Synthesis by Substituent Modification		304
10.8.4.1	Method 1:	Benzo[<i>c</i>]selenophen-1(3 <i>H</i>)-one by Hydrolysis of Benzo[<i>c</i>]selenophen-1(3 <i>H</i>)-imine	304
10.8.4.2	Method 2:	Benzo[<i>c</i>]selenophene-1(3 <i>H</i>)-thione by Reaction of Benzo[<i>c</i>]selenophen-1(3 <i>H</i>)-imine with Hydrogen Sulfide	304
10.9	Product Class 9: Dibenzoselenophenes		
	P. J. Murphy		
10.9	Product Class 9: Dibenzoselenophenes		
10.9.1	Synthesis by Ring-Closure Reactions		307
10.9.1.1	By Annulation to an Arene		307
10.9.1.1.1	By Formation of Two Se—C Bonds and One C—C Bond		307

10.9.1.1.1	Method 1: Miscellaneous Preparations	307
10.9.1.1.2	By Formation of Two Se—C Bonds	308
10.9.1.1.2.1	Method 1: From Biphenyls	308
10.9.1.1.2.2	Method 2: From Metalated Biphenyls	308
10.9.1.1.2.3	Method 3: From 2,2'-Diiodobiphenyls	309
10.9.1.1.3	By Formation of One Se—C and One C—C Bond	310
10.9.1.1.3.1	Method 1: By Photoirradiation	310
10.9.1.1.4	By Formation of One Se—C Bond	310
10.9.1.1.4.1	Method 1: By Intramolecular Electrophilic Aromatic Substitution of Selenenyl Halides	310
10.9.1.1.4.2	Method 2: By Intramolecular Electrophilic Aromatic Substitution of Selenides	311
10.9.1.1.4.3	Method 3: By Intramolecular Electrophilic Aromatic Substitution of Biphenyl-2-yl Trifluoromethyl Selenides and Selenoxides	312
10.9.1.1.4.4	Method 4: Miscellaneous Preparations	312
10.9.1.1.5	By Formation of One C—C Bond	313
10.9.1.1.5.1	Method 1: From Dimetalated Diphenyl Selenides	313
10.9.1.1.5.2	Method 2: Miscellaneous Preparations	313
10.9.1.2	By Annulation to the Heterocyclic Ring	314
10.9.1.2.1	Method 1: By Annulation to Benzo[<i>b</i>]selenophenes	314
10.9.1.2.2	Method 2: By Formylation of a Benzo[<i>b</i>]selenophene and Cyclization	314
10.9.2	Synthesis by Ring Transformation	315
10.9.2.1	Method 1: Miscellaneous Preparations	315
10.9.3	Aromatization	316
10.9.3.1	Method 1: By the Fischer Indole Synthesis	316
10.9.4	Synthesis by Substituent Modification	316
10.9.4.1	Addition Reactions	316
10.9.4.1.1	Method 1: Oxidation at Selenium	316
10.9.4.1.2	Method 2: Imidation at Selenium	317
10.9.4.1.3	Method 3: Halogenation at Selenium	317
10.9.4.2	Substitution of Existing Substituents	318
10.9.4.2.1	Of Hydrogen	318
10.9.4.2.1.1	Method 1: Metalation	318
10.9.4.2.1.2	Method 2: Friedel–Crafts and Related Reactions	318
10.9.4.2.1.2.1	Variation 1: Intermolecular Friedel–Crafts Reactions	318
10.9.4.2.1.2.2	Variation 2: Intramolecular Friedel–Crafts Reactions	319
10.9.4.2.1.3	Method 3: Halogenation and Nitration	320
10.9.4.2.2	Of Metals	321
10.9.4.2.2.1	Method 1: Electrophilic Substitution of Lithium	321

10.9.4.2.3	Of Carbon Functionalities	321
10.9.4.2.3.1	Method 1: Substitution of Carbon Functionalities at Selenium	321
10.9.4.2.4	Of Heteroatoms	322
10.9.4.2.4.1	Method 1: Displacement of Heteroatoms at Selenium	322
10.9.4.3	Modification of Substituents	322
10.10	Product Class 10: Benzo[<i>b</i>]tellurophenes P. J. Murphy	
<hr/>		
10.10	Product Class 10: Benzo[<i>b</i>]tellurophenes	325
10.10.1	Synthesis by Ring-Closure Reactions	325
10.10.1.1	By Annulation to an Arene	325
10.10.1.1.1	By Formation of Two Te—C Bonds	325
10.10.1.1.1.1	Method 1: From 1-Arylalk-1-ynes and Tellurium Dioxide	325
10.10.1.1.1.2	Method 2: From 1-Arylalk-1-ynes and Tellurium Tetrahalides	326
10.10.1.1.1.3	Method 3: From Metalated Intermediates	327
10.10.1.1.1.3.1	Variation 1: From 1-Arylalk-1-ynes	327
10.10.1.1.1.3.2	Variation 2: From 1-(2-Bromophenyl)alk-1-ynes	328
10.10.1.1.1.3.3	Variation 3: From 1-Bromo-2-phenyl- or 1-Bromo-2-(2-bromophenyl)-1-(trimethylsilyl)ethene	329
10.10.1.1.1.3.4	Variation 4: From Bis(2-bromophenyl)acetylene	330
10.10.1.1.2	By Formation of One Te—C Bond	330
10.10.1.1.2.1	Method 1: By Electrophilic Substitution of Styrenes	330
10.10.1.1.2.2	Method 2: Benzo[<i>b</i>]tellurophen-3(2 <i>H</i>)-one from 2-Acetylbenzenetellurenyl Bromide	330
10.10.1.1.2.3	Method 3: Benzo[<i>b</i>]tellurophen-3(2 <i>H</i>)-one from 1-[2-(Butyltellanyl)phenyl]-2-diazoethan-1-one	331
10.10.1.1.3	By Formation of One C—C Bond	331
10.10.1.1.3.1	Method 1: From Intramolecular Condensations with Aldehydes and Ketones	331
10.10.1.1.3.2	Method 2: From Intramolecular Condensations of Dicarboxylic Acids	332
10.10.2	Synthesis by Ring Transformation	333
10.10.2.1	Method 1: By Oxidative Ring Contraction	333
10.10.3	Aromatization	333
10.10.3.1	Method 1: By Dehydrogenation	333
10.10.4	Synthesis by Substituent Modification	334
10.10.4.1	Addition Reactions	334
10.10.4.1.1	Method 1: Alkylation Reactions at Tellurium	334
10.10.4.1.2	Method 2: Halogenation Reactions at Tellurium	334

10.10.4.2	Substitution of Existing Substituents	335
10.10.4.2.1	Of Hydrogen	335
10.10.4.2.1.1	Method 1: Lithiation	335
10.10.4.2.1.2	Method 2: Friedel–Crafts and Related Reactions	335
10.10.4.2.1.3	Method 3: Halogenation	336
10.10.4.2.2	Of Metals	336
10.10.4.2.2.1	Method 1: Substitution of Lithium	336
10.10.4.2.3	Of Carbon Functionalities	337
10.10.4.2.3.1	Method 1: Decarboxylation	337
10.10.4.2.4	Of Heteroatoms	338
10.10.4.2.4.1	Method 1: Reduction of Benzo[<i>b</i>]tellurophen-3(2 <i>H</i>)-one	338
10.10.4.2.4.2	Method 2: Reaction of Benzo[<i>b</i>]tellurophen-3(2 <i>H</i>)-one with Carbon Nucleophiles	338
10.10.4.2.4.3	Method 3: Reaction of Benzo[<i>b</i>]tellurophen-3(2 <i>H</i>)-one with Amine Derivatives	339
10.10.4.2.4.4	Method 4: Reaction of Benzo[<i>b</i>]tellurophen-3(2 <i>H</i>)-one with Halogenating Reagents	339
10.10.4.2.4.5	Method 5: Nucleophilic Substitution of Halogenated Benzo[<i>b</i>]tellurophenes	339
10.10.4.3	Modification of Substituents	340
10.11	Product Class 11: Benzo[<i>c</i>]tellurophenes P. J. Murphy	
10.11	Product Class 11: Benzo[<i>c</i>]tellurophenes	343
10.11.1	Synthesis by Ring-Closure Reactions	343
10.11.1.1	By Annulation to an Arene	343
10.11.1.1.1	By Formation of Two Te–C Bonds	343
10.11.1.1.1.1	Method 1: From 2-(Bromomethyl)benzoyl Halides	343
10.11.1.1.2	By Formation of One Te–C Bond	344
10.11.1.1.2.1	Method 1: From 2-(Bromocarbonyl)benzyltellurenyl Bromide	344
10.11.2	Aromatization	344
10.11.2.1	Method 1: By Elimination	344
10.11.3	Synthesis by Substituent Modification	345
10.11.3.1	Method 1: Benzo[<i>c</i>]tellurophene-1(3 <i>H</i>)-thione by Sulfurization of Benzo[<i>c</i>]tellurophen-1(3 <i>H</i>)-one	345

10.12	Product Class 12: Dibenzotellurophenes P. J. Murphy	
<hr/>		
10.12	Product Class 12: Dibenzotellurophenes	347
10.12.1	Synthesis by Ring-Closure Reactions	347
10.12.1.1	By Annulation to an Arene	347
10.12.1.1.1	By Formation of Two Te—C Bonds and One C—C Bond	347
10.12.1.1.1.1	Method 1: From 1,2-Diodobenzenes and Tellurium	347
10.12.1.1.2	By Formation of Two Te—C Bonds	348
10.12.1.1.2.1	Method 1: From Biphenyls and Inorganic Tellurium Reagents	348
10.12.1.1.2.2	Method 2: From Metalated Biphenyls	349
10.12.1.1.2.3	Method 3: From 2,2'-Diodobiphenyls	350
10.12.1.1.3	By Formation of One Te—C Bond	351
10.12.1.1.3.1	Method 1: By Intramolecular Electrophilic Aromatic Substitution of Biphenyl-2-yltellurium Trichloride	351
10.12.1.1.3.2	Method 2: By Intramolecular Electrophilic Aromatic Substitution of Biphenyl-2-yl Trifluoromethyl Telluride	351
10.12.2	Synthesis by Ring Transformation	352
10.12.2.1	Method 1: Miscellaneous Preparations	352
10.12.3	Synthesis by Substituent Modification	352
10.12.3.1	Addition Reactions	352
10.12.3.1.1	Method 1: Oxidation at Tellurium	352
10.12.3.1.2	Method 2: Imidation at Tellurium	353
10.12.3.1.3	Method 3: Alkylation at Tellurium	353
10.12.3.1.4	Method 4: Halogenation at Tellurium	353
10.12.3.2	Substitution of Existing Substituents	354
10.12.3.2.1	Of Hydrogen	354
10.12.3.2.1.1	Method 1: Nitration and Sulfonation	354
10.12.3.2.2	Of Carbon Functionalities	355
10.12.3.2.2.1	Method 1: Cleavage of the Te—C Bond in Bis(biphenyl-2,2'-diyl)- λ^4 -tellanes	355
10.12.3.2.3	Of Heteroatoms	355
10.12.3.2.3.1	Method 1: Hydrolysis of <i>N</i> -Tosyldibenzotellurophen-5-imine	355
10.12.3.2.3.2	Method 2: Hydrolysis of 5,5-Dichlorodibenzotellurophenes	356
10.12.3.2.3.3	Method 3: Substitution of Halides and Alkoxides at Tellurium	356
10.12.3.2.3.4	Method 4: Bis(biphenyl-2,2'-diyl)- λ^4 -tellane by Substitution at Tellurium	357
10.12.3.3	Modification of Substituents	357
10.12.3.4	Miscellaneous Reactions	357

10.13	Product Class 13: Indole and Its Derivatives	
	J. A. Joule	
10.13	Product Class 13: Indole and Its Derivatives	361
10.13.1	Product Subclass 1: Indoles	361
10.13.1.1	Synthesis by Ring-Closure Reactions	366
10.13.1.1.1	By Annulation to an Arene	366
10.13.1.1.1.1	By Formation of One N—C and One C—C Bond	366
10.13.1.1.1.1.1	With Formation of 1—2 and 3—3a Bonds	366
10.13.1.1.1.1.1.1	Method 1: From Arylhydrazones; Fischer Synthesis	366
10.13.1.1.1.1.1.1.1	Variation 1: From 4-Chlorobutanal and Arylhydrazines; Grandberg Tryptamine Synthesis	377
10.13.1.1.1.1.1.1.2	Variation 2: From β -Oxo Esters and Arenediazonium Ions; Japp–Klingemann Synthesis	378
10.13.1.1.1.1.1.2	Method 2: From <i>O</i> -Alkenyl <i>N</i> -Arylhydroxylamines	380
10.13.1.1.1.1.3	Method 3: From <i>ortho</i> -Substituted Nitroarenes; Bartoli Synthesis	384
10.13.1.1.1.1.4	Method 4: From Arylamines and Alkylsulfanylmethyl Ketones; Gassman Indole Synthesis	387
10.13.1.1.1.1.5	Method 5: From Arylamines and Ketones	389
10.13.1.1.1.1.6	Method 6: From Arylamines and 1,2-Diols	389
10.13.1.1.1.1.7	Method 7: From Arylamines and α -Halo Ketones; Bischler Synthesis	390
10.13.1.1.1.1.8	Method 8: From <i>o</i> -Iodoarylamines and Alkynes	391
10.13.1.1.1.1.9	Method 9: From <i>N</i> -Acyl- <i>o</i> -bromoarylamines and α -Halo Ketones	392
10.13.1.1.1.1.10	Method 10: From <i>ortho</i> -Thallated <i>N</i> -Acylarylamines and 3-Chloroprop-1-ene	393
10.13.1.1.1.1.11	Method 11: From <i>N</i> -Alkyl- <i>N</i> -arylhydroxylamines and Alkynes Carrying Electron-Withdrawing Groups	394
10.13.1.1.1.1.12	Method 12: From <i>N</i> -Sulfinylarylamines and Grignard Reagents	394
10.13.1.1.1.1.13	Method 13: From <i>N</i> -Arylarenesulfonamides and Phenyl(propynyl)iodonium Triflate	395
10.13.1.1.1.2	With Formation of 1—2 and 2—3 Bonds	395
10.13.1.1.1.2.1	Method 1: From <i>o</i> -Alkylarylamines	395
10.13.1.1.1.2.2	Method 2: From <i>o</i> -Acylarylamines	399
10.13.1.1.1.2.3	Method 3: From 1-(<i>o</i> -Aminoaryl)alkenes	400
10.13.1.1.1.3	With Formation of 1—7a and 3—3a Bonds	401
10.13.1.1.1.3.1	Method 1: From Benzo-1,4-quinones and Enamines; Nenitzescu Synthesis	401
10.13.1.1.1.4	With Formation of 1—7a and 1—2 Bonds	403
10.13.1.1.1.4.1	Method 1: From 1-(<i>m</i> -Hydroxyaryl)alkenes	403
10.13.1.1.2	By Formation of One N—C Bond	404
10.13.1.1.2.1	With Formation of the 1—2 Bond	404

10.13.1.1.1.2.1.1	Method 1:	From α -(<i>o</i> -Aminoaryl) Ketones, 2-(<i>o</i> -Aminoaryl)aldehydes, or Synthons Thereof	404
10.13.1.1.1.2.1.1.1	Variation 1:	From (<i>o</i> -Aminoaryl)pyruvates [3-(<i>o</i> -Aminoaryl)-2-oxopropanoates]; Reissert Synthesis	405
10.13.1.1.1.2.1.1.2	Variation 2:	From α -(<i>o</i> -Aminoaryl) Ketones	407
10.13.1.1.1.2.1.1.3	Variation 3:	From 2-(<i>o</i> -Aminoaryl)acetaldehydes	415
10.13.1.1.1.2.1.1.4	Variation 4:	From 2-(<i>o</i> -Aminoaryl)acetaldehyde Acetals or Hemiacetals	417
10.13.1.1.1.2.1.1.5	Variation 5:	From 2-(<i>o</i> -Amidoaryl)enol Ethers and 2-(<i>o</i> -Nitroaryl)enol Ethers	420
10.13.1.1.1.2.1.1.6	Variation 6:	From 2-(<i>o</i> -Nitroaryl)enamines; Leimgruber–Batcho Synthesis	421
10.13.1.1.1.2.1.1.7	Variation 7:	From 1-Nitro-2-(<i>o</i> -nitroaryl)ethenes	426
10.13.1.1.1.2.1.2	Method 2:	From <i>o</i> -Alkynylarylamines	428
10.13.1.1.1.2.1.3	Method 3:	From <i>o</i> -Alkenylnitroarenes and <i>o</i> -Alkenylaryl Azides	432
10.13.1.1.1.2.1.4	Method 4:	From <i>o</i> -Alkenylarylamines and <i>N</i> -Acyl Derivatives Thereof	435
10.13.1.1.1.2.1.5	Method 5:	From <i>o</i> -Acetamidoaryl Alkynyl Carbinols	437
10.13.1.1.1.2.1.6	Method 6:	From (<i>o</i> -Nitroaryl)acetonitriles	437
10.13.1.1.1.2.1.7	Method 7:	From <i>o</i> -(Chloroacetyl)arylamines; Sugasawa Synthesis	438
10.13.1.1.1.2.2	With Formation of the 1–7a Bond		439
10.13.1.1.1.2.2.1	Method 1:	From 2-Arylalkenyl Azides; Hemetsberger–Knittel Synthesis	439
10.13.1.1.1.2.2.2	Method 2:	From 2-(<i>o</i> -Haloaryl)-2-hydroxyethanamines	440
10.13.1.1.1.2.2.3	Method 3:	From 1-(<i>m</i> -Hydroxyaryl)alkan-2-amines	441
10.13.1.1.1.3	By Formation of One C–C Bond		443
10.13.1.1.1.3.1	With Formation of the 2–3 Bond		443
10.13.1.1.1.3.1.1	Method 1:	From <i>N</i> -(<i>o</i> -Methylaryl)amides; Madelung Synthesis	443
10.13.1.1.1.3.1.1.1	Variation 1:	From <i>N</i> -[<i>o</i> -(Acylmethyl)-, <i>N</i> -[<i>o</i> -(Cyanomethyl)-, <i>N</i> -[<i>o</i> -(Alkoxy carbonylmethyl)-, or <i>N</i> -[<i>o</i> -(Phenylsulfonylmethyl)aryl]amides	445
10.13.1.1.1.3.1.1.2	Variation 2:	From [(<i>o</i> -Acylaminoaryl)methyl]phosphonium Salts	446
10.13.1.1.1.3.1.1.3	Variation 3:	From [(<i>o</i> -Acylaminoaryl)methyl]silanes	449
10.13.1.1.1.3.1.2	Method 2:	From <i>o</i> -Acylarylamines	449
10.13.1.1.1.3.1.3	Method 3:	From <i>o</i> -Alkylaryl Isocyanides	451
10.13.1.1.1.3.1.4	Method 4:	From <i>o</i> -Alkenylaryl Isocyanides; Fukuyama Synthesis	455
10.13.1.1.1.3.1.5	Method 5:	From <i>N</i> -(<i>o</i> -Acylaryl)amides; Fürstner Synthesis	456
10.13.1.1.1.3.1.6	Method 6:	From <i>N</i> -(<i>o</i> -Alkylaryl)imidates and -imines	459
10.13.1.1.1.3.2	With Formation of the 3–3a Bond		461
10.13.1.1.1.3.2.1	Method 1:	From 2-(Arylamino)aldehydes and α -(Arylamino) Ketones or Synthons Thereof	461
10.13.1.1.1.3.2.2	Method 2:	From 3-Arylamino-1-(trialkylsilyl)prop-1-yne	463
10.13.1.1.1.3.2.3	Method 3:	From (<i>o</i> -Haloarylamino)alkenes	463
10.13.1.1.1.3.2.4	Method 4:	From Arylaminoalkenes	465
10.13.1.1.1.3.2.5	Method 5:	From <i>N</i> -(<i>o</i> -Haloaryl)prop-2-ynylamines	466
10.13.1.1.1.3.2.6	Method 6:	From <i>N</i> -(<i>o</i> -Haloaryl)allylamines	467
10.13.1.1.1.3.2.7	Method 7:	From <i>N</i> -(<i>m</i> -Haloaryl)imines	468
10.13.1.1.1.3.2.8	Method 8:	From 1-Aryl-1,2,3-triazoles	469
10.13.1.1.1.3.2.9	Method 9:	From <i>N</i> -Arylethanolamines	470

10.13.1.1.1.3.2.10	Method 10: From <i>N</i> -Aryl-2-chloroallylamines	471
10.13.1.1.1.3.2.11	Method 11: From <i>N</i> -(2-Aminoaryl)-2-bromo- <i>N</i> -mesylallylamines	472
10.13.1.1.2	By Annulation to a Pyrrole	472
10.13.1.1.2.1	By Formation of Three C—C Bonds	472
10.13.1.1.2.1.1	With Formation of 3a—4, 4—5, and 6—7 Bonds	472
10.13.1.1.2.1.1.1	Method 1: From Pyrrole Carbene Chromium Complexes	472
10.13.1.1.2.2	By Formation of Two C—C Bonds	474
10.13.1.1.2.2.1	With Formation of 3a—4 and 5—6 Bonds	474
10.13.1.1.2.2.1.1	Method 1: From 2-Alkenylpyrroles	474
10.13.1.1.2.2.2	With Formation of 5—6 and 7—7a Bonds	475
10.13.1.1.2.2.2.1	Method 1: From 3-Alkenylpyrroles	475
10.13.1.1.2.2.3	With Formation of 3a—4 and 7—7a Bonds	477
10.13.1.1.2.2.3.1	Method 1: From Pyrroles and 1,4-Diones	477
10.13.1.1.2.2.4	With Formation of 3a—4 and 4—5 Bonds	478
10.13.1.1.2.2.4.1	Method 1: From 2-(3-Acyloxyprop-1-enyl)pyrroles and Carbon Monoxide	478
10.13.1.1.2.3	By Formation of One C—C Bond	478
10.13.1.1.2.3.1	With Formation of the 3a—4 Bond	478
10.13.1.1.2.3.1.1	Method 1: From Pyrroles with a C ₄ -Chain at C2	478
10.13.1.1.2.3.2	With Formation of the 7—7a Bond	482
10.13.1.1.2.3.2.1	Method 1: From Pyrroles with a C ₄ -Chain at C3	482
10.13.1.1.2.3.3	With Formation of the 5—6 Bond	485
10.13.1.1.2.3.3.1	Method 1: From 2-Acyl-3-(2-haloaryl)pyrroles	485
10.13.1.1.2.3.3.2	Method 2: From Alk-2-enyl-1-methyl-4-nitro-3-styrylpyrroles	486
10.13.1.2	Synthesis by Ring Transformation	486
10.13.1.2.1	Method 1: From Other Heterocyclic Systems	486
10.13.1.3	Aromatization	489
10.13.1.3.1	Method 1: Dehydrogenation of 2,3-Dihydro-1 <i>H</i> -indoles	489
10.13.1.3.2	Method 2: Dehydrogenation of Benzene Ring Reduced Indoles	492
10.13.1.3.3	Method 3: Reduction and Other Transformations of 1 <i>H</i> -Indole-2,3-diones (Isatins), 1,2-Dihydro-3 <i>H</i> -indol-3-ones (Indoxyls), 1 <i>H</i> -Indol-1-ols, and 1,3-Dihydro-2 <i>H</i> -indol-2-ones (Oxindoles)	493
10.13.1.4	Synthesis by Substitution of Existing Substituents	494
10.13.1.4.1	Substitution of <i>N</i> -Hydrogen	494
10.13.1.4.1.1	Method 1: Giving <i>N</i> -Halogen Indoles	494
10.13.1.4.1.2	Method 2: Giving <i>N</i> -Nitrogen Indoles	495
10.13.1.4.1.3	Method 3: Giving <i>N</i> -Phosphorus Indoles	495
10.13.1.4.1.4	Method 4: Giving <i>N</i> -Carbon Indoles	495

10.13.1.4.1.5	Method 5: Giving <i>N</i> -Metal Indoles	499
10.13.1.4.2	Substitution of <i>C</i> -Hydrogen	499
10.13.1.4.2.1	Electrophilic Substitution	499
10.13.1.4.2.1.1	On the Five-Membered Ring	499
10.13.1.4.2.1.1.1	Method 1: Giving <i>C</i> -Deuterium/Tritium Indoles	499
10.13.1.4.2.1.1.2	Method 2: Giving <i>C</i> -Halogen Indoles	500
10.13.1.4.2.1.1.3	Method 3: Giving <i>C</i> -Sulfur Indoles	502
10.13.1.4.2.1.1.4	Method 4: Giving <i>C</i> -Nitrogen Indoles	505
10.13.1.4.2.1.1.5	Method 5: Giving <i>C</i> -Carbon Indoles	506
10.13.1.4.2.1.1.5.1	Variation 1: Introduction of Carboxy and Cyano Groups	506
10.13.1.4.2.1.1.5.2	Variation 2: Introduction of Acyl Groups	507
10.13.1.4.2.1.1.5.3	Variation 3: Introduction of Hydroxyalkyl and Related Groups	513
10.13.1.4.2.1.1.5.4	Variation 4: Introduction of Aminoalkyl Groups	517
10.13.1.4.2.1.1.5.5	Variation 5: Introduction of Sulfanylalkyl Groups	523
10.13.1.4.2.1.1.5.6	Variation 6: Introduction of Alkyl Groups	523
10.13.1.4.2.1.1.6	Method 6: Giving <i>C</i> -Silicon Indoles	533
10.13.1.4.2.1.1.7	Method 7: Giving <i>C</i> -Mercury Indoles	533
10.13.1.4.2.1.1.8	Method 8: Giving <i>C</i> -Thallium Indoles	533
10.13.1.4.2.1.1.9	Method 9: Giving <i>C</i> -Palladium Indoles	533
10.13.1.4.2.1.2	On the Benzene Ring	534
10.13.1.4.2.1.2.1	Method 1: Substitution of Indoles	534
10.13.1.4.2.1.2.2	Method 2: Substitution of 2,3-Dihydro-1 <i>H</i> -indoles (Indolines)	537
10.13.1.4.2.2	Nucleophilic Substitution	541
10.13.1.4.2.2.1	Method 1: Giving <i>C</i> -Oxygen Indoles	541
10.13.1.4.2.2.2	Method 2: Giving <i>C</i> -Nitrogen Indoles	543
10.13.1.4.2.2.3	Method 3: Giving <i>C</i> -Carbon Indoles	544
10.13.1.4.2.3	Radical Substitution	546
10.13.1.4.2.3.1	Method 1: Giving <i>C</i> -Carbon Indoles	546
10.13.1.4.2.3.2	Method 2: Giving <i>C</i> -Tin Indoles	548
10.13.1.4.2.4	Base Deprotonation	548
10.13.1.4.2.4.1	Method 1: Giving <i>C</i> -Lithium Indoles	548
10.13.1.4.3	Substitution of <i>N</i> -Metal	552
10.13.1.4.3.1	Giving <i>N</i> -Substituted Products	552
10.13.1.4.3.1.1	Method 1: Giving <i>N</i> -Halogen Indoles	552
10.13.1.4.3.1.2	Method 2: Giving <i>N</i> -Sulfur Indoles	552
10.13.1.4.3.1.3	Method 3: Giving <i>N</i> -Nitrogen Indoles	553
10.13.1.4.3.1.4	Method 4: Giving <i>N</i> -Carbon Indoles	554
10.13.1.4.3.1.4.1	Variation 1: Introduction of Carboxy, Cyano, and Related Groups	554
10.13.1.4.3.1.4.2	Variation 2: Introduction of Acyl Groups	554
10.13.1.4.3.1.4.3	Variation 3: Introduction of Alkenyl Groups	556
10.13.1.4.3.1.4.4	Variation 4: Introduction of Aryl Groups	556
10.13.1.4.3.1.4.5	Variation 5: Introduction of Alkyl Groups	556

10.13.1.4.3.1.5	Method 5: Giving Other <i>N</i> -Metal Indoles	560
10.13.1.4.3.2	Giving <i>C</i> -Substituted Products	560
10.13.1.4.3.2.1	Method 1: Giving <i>C</i> -Halogen Indoles	560
10.13.1.4.3.2.2	Method 2: Giving <i>C</i> -Sulfur Indoles	561
10.13.1.4.3.2.3	Method 3: Giving <i>C</i> -Nitrogen Indoles	561
10.13.1.4.3.2.4	Method 4: Giving <i>C</i> -Carbon Indoles	562
10.13.1.4.4	Substitution of <i>C</i> -Metal	565
10.13.1.4.4.1	Method 1: Giving <i>C</i> -Halogen Indoles	565
10.13.1.4.4.2	Method 2: Giving <i>C</i> -Oxygen Indoles	566
10.13.1.4.4.3	Method 3: Giving <i>C</i> -Sulfur Indoles	566
10.13.1.4.4.4	Method 4: Giving <i>C</i> -Nitrogen Indoles	566
10.13.1.4.4.5	Method 5: Giving <i>C</i> -Carbon Indoles	567
10.13.1.4.4.5.1	Variation 1: Reactions with Carbon Electrophiles	567
10.13.1.4.4.5.2	Variation 2: Via Reactions with Boron Electrophiles	567
10.13.1.4.4.5.3	Variation 3: Via <i>Ipso</i> Displacement of Silicon	569
10.13.1.4.4.5.4	Variation 4: Via Organopalladium Intermediates Using Metalated Indoles	570
10.13.1.4.4.5.5	Variation 5: Organopalladium Intermediates Using Indole Halides and Triflates	575
10.13.1.4.4.5.6	Variation 6: Synthetic Applications of Hapto Metal Complexes of Indoles	577
10.13.1.4.4.6	Method 6: Giving Other <i>C</i> -Metal Indoles	578
10.13.1.5	Synthesis by Substituent Modification	579
10.13.1.5.1	Modification of <i>N</i> -Carbon Functionalities	579
10.13.1.5.1.1	Method 1: Giving <i>N</i> -Hydrogen Indoles	579
10.13.1.5.1.2	Method 2: Giving <i>N</i> -Carbon Indoles	579
10.13.1.5.2	Modification of <i>C</i> -Carbon Functionalities	581
10.13.1.5.2.1	Method 1: Giving <i>C</i> -Hydrogen Indoles	581
10.13.1.5.2.2	Method 2: Giving <i>C</i> -Oxygen Indoles	582
10.13.1.5.2.3	Method 3: Giving <i>C</i> -Nitrogen Indoles	582
10.13.1.5.2.4	Method 4: Giving <i>C</i> -Carbon Indoles	582
10.13.1.5.3	Modification of <i>N</i> -Heteroatom Functionality	591
10.13.1.5.3.1	Method 1: Modification of <i>N</i> -Sulfur Functionality	591
10.13.1.5.3.2	Method 2: Modification of <i>N</i> -Silicon Functionality	591
10.13.1.5.4	Modification of <i>C</i> -Heteroatom Functionality	591
10.13.1.5.4.1	Method 1: Of <i>C</i> -Halogen Indoles	591
10.13.1.5.4.2	Method 2: Of <i>C</i> -Oxygen Indoles	592
10.13.1.5.4.3	Method 3: Of <i>C</i> -Sulfur Indoles	592
10.13.1.5.4.4	Method 4: Of <i>C</i> -Nitrogen Indoles	592
10.13.1.5.4.5	Method 5: Of <i>C</i> -Silicon Indoles	592
10.13.1.5.5	Rearrangement of <i>N</i> -Substituents	593
10.13.1.5.5.1	Method 1: Giving <i>C</i> -Halogen Indoles	593
10.13.1.5.5.2	Method 2: Giving <i>C</i> -Carbon Indoles	593

10.13.1.5.6	Rearrangement of C-Substituents	593
10.13.1.5.6.1	Method 1: Giving C-Nitrogen Indoles	593
10.13.1.5.6.2	Method 2: Giving C-Carbon Indoles	593
10.13.2	Product Subclass 2: 1H-Indol-1-ols (1-Hydroxy-1H-indoles)	594
10.13.2.1	Synthesis by Ring-Closure Reactions	596
10.13.2.1.1	By Annulation to an Arene	596
10.13.2.1.1.1	By Formation of One N—C Bond	596
10.13.2.1.1.1.1	With Formation of the 1—2 Bond	596
10.13.2.1.1.1.1.1	Method 1: From (Arylmethyl)(<i>o</i> -nitroaryl)acetonitriles	596
10.13.2.1.1.1.1.2	Method 2: From 2-(<i>o</i> -Nitroaryl)enamines	597
10.13.2.1.1.1.1.3	Method 3: From 2-(<i>o</i> -Nitroaryl)acetic Acids and Esters	598
10.13.2.1.1.1.2	With Formation of the 1—7a Bond	598
10.13.2.1.1.1.2.1	Method 1: From 1-Aryl-2-nitroalkenes	598
10.13.2.2	Aromatization	599
10.13.2.2.1	Method 1: Oxidation of 2,3-Dihydro-1H-indoles (Indolines)	599
10.13.2.2.2	Method 2: Reduction of 1-Hydroxy-1,3-dihydro-2H-indol-2-ones	599
10.13.3	Product Subclass 3: 1,3-Dihydro-2H-indol-2-ones (1H-Indol-2-ols, 2-Hydroxy-1H-indoles, or Oxindoles)	600
10.13.3.1	Synthesis by Ring-Closure Reactions	603
10.13.3.1.1	By Annulation to an Arene	603
10.13.3.1.1.1	By Formation of One N—C and One C—C Bond	603
10.13.3.1.1.1.1	With Formation of 1—2 and 3—3a Bonds	603
10.13.3.1.1.1.1.1	Method 1: From Arylamines and an α -(Alkylsulfanyl) Ester	603
10.13.3.1.1.1.1.1.1	Variation 1: From Arylamines and (Methylsulfanyl) Acetates	603
10.13.3.1.1.1.1.2	Method 2: From Arylhydrazides; Brunner Synthesis	604
10.13.3.1.1.1.1.3	Method 3: From Arylaminoalkynes	605
10.13.3.1.1.1.2	With Formation of 1—2 and 2—3 Bonds	606
10.13.3.1.1.1.2.1	Method 1: From <i>N</i> -Protected <i>o</i> -Alkylanilines	606
10.13.3.1.1.1.2.2	Method 2: From <i>o</i> -Alkynylanilines	607
10.13.3.1.1.2	By Formation of One N—C Bond	607
10.13.3.1.1.2.1	With Formation of the 1—2 Bond	607
10.13.3.1.1.2.1.1	Method 1: From (<i>o</i> -Nitroaryl)acetic Acids and Esters	607
10.13.3.1.1.2.1.2	Method 2: From <i>N,O</i> -Diacylarylhydroxylamines	608
10.13.3.1.1.2.1.3	Method 3: From Nitroarenes	609
10.13.3.1.1.2.1.4	Method 4: From (<i>o</i> -Nitroaryl)pyruvates [3-(<i>o</i> -Nitroaryl)-2-oxopropanoates]	609
10.13.3.1.1.2.1.5	Method 5: From (<i>o</i> -Nitroaryl)acetonitriles	610
10.13.3.1.1.2.2	With Formation of the 1—7a Bond	611
10.13.3.1.1.2.2.1	Method 1: From (<i>o</i> -Haloaryl)acetamides	611

10.13.3.1.1.2.2.2	Method 2: From <i>N</i> -Methoxyarylacetamides	611
10.13.3.1.1.3	By Formation of One C—C Bond	612
10.13.3.1.1.3.1	With Formation of the 3—3a Bond	612
10.13.3.1.1.3.1.1	Method 1: From <i>N</i> -Arylchloroacetamides and Related Amides	612
10.13.3.1.1.3.1.2	Method 2: From 2-(Alkoxy carbonyl)- or 2-Acyl- <i>N</i> -aryl-2-diazoacetamides	614
10.13.3.1.1.3.1.3	Method 3: From <i>N</i> -Aryltrichloroacetamides	615
10.13.3.1.1.3.1.4	Method 4: From <i>N</i> -(<i>o</i> -Haloaryl)alkanamides	615
10.13.3.1.1.3.1.5	Method 5: From α,β -Unsaturated <i>N</i> -(<i>o</i> -Haloaryl)alkanamides	616
10.13.3.2	Synthesis by Substituent Modification	617
10.13.3.2.1	Method 1: Oxidation of Indoles	617
10.13.3.2.2	Method 2: Reduction of 1 <i>H</i> -Indole-2,3-diones (Isatins)	619
10.13.4	Product Subclass 4: 1,2-Dihydro-3<i>H</i>-indol-3-ones (1<i>H</i>-Indol-3-ols, 3-Hydroxy-1<i>H</i>-indoles, or Indoxyls)	619
10.13.4.1	Synthesis by Ring-Closure Reactions	620
10.13.4.1.1	By Annulation to an Arene	620
10.13.4.1.1.1	By Formation of One N—C and One C—C Bond	620
10.13.4.1.1.1.1	With Formation of 1—2 and 3—3a Bonds	620
10.13.4.1.1.1.1.1	Method 1: From Arylamines and Glyoxal Derivatives	620
10.13.4.1.1.2	By Formation of One N—C Bond	621
10.13.4.1.1.2.1	With Formation of the 1—2 Bond	621
10.13.4.1.1.2.1.1	Method 1: From 1-(<i>o</i> -Aminoaryl)allyl Silyl Ethers	621
10.13.4.1.1.2.1.2	Method 2: From <i>o</i> -Aminoaryl Halomethyl Ketones; Sugasawa Indoxyl Synthesis	621
10.13.4.1.1.3	By Formation of One C—C Bond	622
10.13.4.1.1.3.1	With Formation of the 2—3 Bond	622
10.13.4.1.1.3.1.1	Method 1: From [(<i>o</i> -Carboxyaryl)amino]acetic Acids and [<i>o</i> -(Alkoxy carbonyl)aryl]amino]acetic Acid Esters	622
10.13.4.1.1.3.2	With Formation of the 3—3a Bond	623
10.13.4.1.1.3.2.1	Method 1: From <i>N</i> -Arylglycines	623
10.13.4.2	Synthesis by Substituent Modification	624
10.13.4.2.1	Method 1: Oxidation of Indoles	624
10.14	Product Class 14: 1<i>H</i>- and 2<i>H</i>-Isoindoles T. J. Donohoe	
10.14	Product Class 14: 1<i>H</i>- and 2<i>H</i>-Isoindoles	653
10.14.1	Synthesis by Ring-Closure Reactions	657
10.14.1.1	By Annulation to an Arene	657
10.14.1.1.1	By Formation of Two N—C Bonds	657

10.14.1.1.1.1	Method 1: Synthesis from Dicarbonyl Compounds	657
10.14.1.1.1.1.1	Variation 1: By Condensation	657
10.14.1.1.1.1.2	Variation 2: Reductive Cyclization	658
10.14.1.1.2	By Formation of One N—C and One C—C Bond	659
10.14.1.1.2.1	Method 1: Cyclization onto Aryl Nitriles	659
10.14.1.1.3	By Formation of Two C—C Bonds	660
10.14.1.1.3.1	Method 1: Cycloaddition of Dicyanomethylide Dipoles with Benzyne ...	660
10.14.1.1.3.2	Method 2: Formation of Isoindole-1-carbonitrile From a Dipole	661
10.14.1.1.4	By Formation of One N—C Bond	662
10.14.1.1.4.1	Method 1: Reaction of 2-Substituted Benzonitriles	662
10.14.1.1.4.2	Method 2: Reaction of 2-Substituted Benzylamines	662
10.14.1.1.5	By Formation of One C—C Bond	663
10.14.1.1.5.1	Method 1: Cyclization onto Benzynes	663
10.14.1.2	By Annulation to the Pyrrole Ring	664
10.14.1.2.1	Method 1: Onto Formylpyrroles	664
10.14.1.2.2	Method 2: Onto C3 and C4 of Pyrrole	665
10.14.2	Synthesis by Ring Transformation	666
10.14.2.1	Retrocycloaddition	666
10.14.2.1.1	Method 1: Retro-Diels–Alder Reaction	666
10.14.2.1.2	Method 2: Extrusion Reactions	668
10.14.2.2	Ring Enlargement	669
10.14.2.2.1	Method 1: Ylides as Intermediates	669
10.14.2.3	Ring Contraction	670
10.14.2.3.1	Method 1: Of Isoquinolines	670
10.14.2.3.2	Method 2: Of Benzodiazepines	670
10.14.2.3.3	Method 3: Of Isoquinoline <i>N</i> -Oxide	672
10.14.3	Aromatization	672
10.14.3.1	Method 1: By Dehydrogenation	672
10.14.3.1.1	Variation 1: Of the Heterocyclic Ring	672
10.14.3.1.2	Variation 2: Of the Carbocyclic Ring	673
10.14.3.2	Method 2: By Retro-Ene Reaction	674
10.14.3.3	Method 3: By Elimination	674
10.14.3.3.1	Variation 1: From <i>N</i> -Oxides	674
10.14.3.3.2	Variation 2: From Sulfonamides	676
10.14.3.3.3	Variation 3: By Elimination from Isoindolinium Salts	679
10.14.4	Synthesis by Substituent Modification	680
10.14.4.1	Method 1: Reduction of Phthalimides	680
10.14.4.2	Substitution of Existing Substituents	681
10.14.4.2.1	Of Hydrogen	681

10.14.4.2.1.1	Method 1: Deuteriation	681
10.14.4.2.1.2	Method 2: Alkylation	681
10.14.4.2.1.3	Method 3: Acylation of Isoindoles	683
10.14.4.2.1.4	Method 4: Amination of Isoindoles	685
10.14.4.2.2	Of Carbon Functionalities	686
10.14.4.2.2.1	Method 1: Decarboxylation	686
10.14.4.3	Modification of Substituents	686
10.14.4.3.1	Method 1: Addition to Phthalimidines	686
10.14.4.3.2	Method 2: Condensation of Phthalimidines with Pyridines	687
10.14.4.3.3	Method 3: Alkylation of Phthalimidines	688
10.15	Product Class 15: Carbazoles	
	P. T. Gallagher	
<hr/>		
10.15	Product Class 15: Carbazoles	693
10.15.1	Synthesis By Ring-Closure Reactions	695
10.15.1.1	By Annulation to an Arene	695
10.15.1.1.1	By Formation of Three C—C Bonds	695
10.15.1.1.1.1	Method 1: Intramolecular Tandem Alkyne Insertion–Carbene Annulation	695
10.15.1.1.2	By Formation of Two Heteroatom–Heteroatom Bonds	696
10.15.1.1.2.1	Method 1: Nucleophilic Displacement of Methoxybiaryls Using Ammonia	696
10.15.1.1.3	By Formation of One Heteroatom–Carbon and One C—C Bond	697
10.15.1.1.3.1	Method 1: Reaction between Benzyne and a Nitrosobenzene	697
10.15.1.1.3.2	Method 2: Iodine-Catalyzed Dimerization of Aniline	697
10.15.1.1.3.3	Method 3: Reaction between Anilines and Benzoquinone	698
10.15.1.1.3.4	Method 4: Reaction between 2-Naphthol and Phenylhydrazine	698
10.15.1.1.4	By Formation of Two C—C Bonds	699
10.15.1.1.4.1	With Formation of 1–2 and 3–4 Bonds	699
10.15.1.1.4.1.1	Method 1: Reaction of 1-Methylindole-2,3-dicarbaldehyde and Diketones	699
10.15.1.1.4.1.2	Method 2: Diels–Alder Reactions of Pyrano[3,4- <i>b</i>]indol-3(9 <i>H</i>)-one	700
10.15.1.1.4.1.3	Method 3: Anionic [4+2] Cycloadditions of Indole-2,3-dienolate	700
10.15.1.1.4.1.4	Method 4: Diels–Alder Reactions of 2,4-Dihydropyrrolo[3,4- <i>b</i>]indoles	701
10.15.1.1.4.1.5	Method 5: Reaction between Indole-2,3-quinodimethane and Alkynes	702
10.15.1.1.4.2	With Formation of 1–2 and 4–4a Bonds	702
10.15.1.1.4.2.1	Method 1: Reaction of 2-Ethylindole with But-3-en-2-one	702
10.15.1.1.4.2.2	Method 2: Cyclization of 2-Methylindole with Hydroxymethylene Ketones	703

10.15.1.1.4.3	With Formation of 2–3 and 9a–1 Bonds	703
10.15.1.1.4.3.1	Method 1: Diels–Alder Reactions of Thieno[2,3- <i>b</i>]indoles	703
10.15.1.1.4.3.2	Method 2: Diels–Alder Reactions of 2-(1 <i>H</i> -Indol-3-yl)ethene- 1,1,2-tricarbonitrile	704
10.15.1.1.4.4	With Formation of 3–4 and 9a–1 Bonds	704
10.15.1.1.4.4.1	Method 1: Cyclization of Benzotriazol-1-ylmethylindole with Enones	704
10.15.1.1.4.4.2	Method 2: Cyclization of Indol-3-ylacetonitrile with Perchlorates	705
10.15.1.1.4.5	With Formation of 4–4a and 9a–1 Bonds	706
10.15.1.1.4.5.1	Method 1: Condensation of 1,4-Diketones with Indoles	706
10.15.1.1.4.5.2	Method 2: Synthesis of 2-(2-Aminoethyl)carbazoles	706
10.15.1.1.4.5.3	Method 3: Acid-Catalyzed Condensation of 1-Arylpyrroles with 2,5-Dimethoxytetrahydrofuran	707
10.15.1.1.5	By Formation of One Heteroatom–Carbon Bond	707
10.15.1.1.5.1	Method 1: Deoxygenation of Nitrobiphenyls	708
10.15.1.1.5.2	Method 2: Decomposition of Azidobiphenyls	708
10.15.1.1.5.2.1	Variation 1: Thermolysis of Azidobiphenyls	709
10.15.1.1.5.2.2	Variation 2: Photolysis of Azidobiphenyls	709
10.15.1.1.5.3	Method 3: Cyclization of 2,2'-Diaminobiphenyls	710
10.15.1.1.5.3.1	Variation 1: The Täufer Synthesis of Carbazoles	710
10.15.1.1.5.3.2	Variation 2: Diazotization of 2,2'-Diaminobiphenyls	711
10.15.1.1.5.4	Method 4: Intramolecular Displacement of Bromine with a Sulfonamide	711
10.15.1.1.5.5	Method 5: Oxidative Cyclization of Tricarbonyl(η^4 -1,3-cyclohexadienyl)iron Complexes	711
10.15.1.1.6	By Formation of One C–C Bond	712
10.15.1.1.6.1	With Formation of the 1–2 Bond	712
10.15.1.1.6.1.1	Method 1: Base-Catalyzed Cyclization of 3-Substituted 2-Alkylindoles ..	712
10.15.1.1.6.2	With Formation of the 2–3 Bond	712
10.15.1.1.6.2.1	Method 1: Rearrangement of Divinylindoles	713
10.15.1.1.6.3	With Formation of the 3–4 Bond	713
10.15.1.1.6.3.1	Method 1: Cyclization of Propenylindoles	713
10.15.1.1.6.4	With Formation of the 4–4a Bond	714
10.15.1.1.6.4.1	Method 1: Annulation of Chromium Carbene Complexes	714
10.15.1.1.6.4.2	Method 2: Acid-Catalyzed Cyclization of 1,4-Diketones	714
10.15.1.1.6.4.3	Method 3: Cycloaromatization of Hydroxyketene Dithioacetals	715
10.15.1.1.6.4.4	Method 4: Synthesis from Indolylpyridinium Methiodide	715
10.15.1.1.6.5	With Formation of the 4a–4b Bond	716
10.15.1.1.6.5.1	Method 1: Palladium-Promoted Cyclization of Diphenylamines	716
10.15.1.1.6.5.2	Method 2: Photolytic Cyclization of Diarylamines	717
10.15.1.1.6.5.3	Method 3: The Graebe–Ullmann Synthesis	717

10.15.1.1.6.6	With Formation of the 9a—1 Bond	718
10.15.1.1.6.6.1	Method 1: Cyclization and Dehydrogenation of Indol-3-yldienes	718
10.15.1.1.6.6.2	Method 2: Cyclization and Elimination of Indol-3-yldienes	719
10.15.1.1.6.6.3	Method 3: Cyclization of Indolylbutenoic Acids to Acetoxycarbazoles ...	719
10.15.1.1.6.6.4	Method 4: Cyclization of β -Oxo Sulfoxides	720
10.15.1.1.6.6.5	Method 5: Cyclization of Cyanoindolylpent-3-en-2-ones	720
10.15.2	Synthesis by Ring Transformation	721
10.15.2.1	Method 1: Desulfurization of Phenothiazines	721
10.15.3	Aromatization	721
10.15.3.1	Method 1: Elimination of Sulfite	721
10.15.3.2	Method 2: Reductive Acylation of Quinones	722
10.15.3.3	Method 3: Dehydrogenation of 1,2,3,4-Tetrahydrocarbazoles	722
10.15.3.3.1	Variation 1: With Palladium on Charcoal	723
10.15.3.3.2	Variation 2: With Chloranil	723
10.15.4	Synthesis by Substituent Modification	724
10.15.4.1	Addition Reactions	724
10.15.4.1.1	Method 1: Synthesis of (η^6 -Carbazole)(η^5 -cyclopentadienyl)iron(II) Hexafluorophosphate	724
10.15.4.1.2	Method 2: Synthesis of Carbazole(tricarbonyl)chromium(0)	725
10.15.4.1.3	Method 3: Protonation of Carbazoles	725
10.15.4.2	Substitution of Existing Substituents	725
10.15.4.2.1	Substitution of Hydrogen	725
10.15.4.2.1.1	Method 1: Metalation at Carbon	726
10.15.4.2.1.2	Method 2: Acylation on Carbon	726
10.15.4.2.1.3	Method 3: Formylation of Carbazoles	726
10.15.4.2.1.4	Method 4: Chlorination of 9-Alkylcarbazoles	727
10.15.4.2.1.5	Method 5: Bromination of 9H-Carbazole	727
10.15.4.2.1.6	Method 6: Iodination of 9H-Carbazole	728
10.15.4.2.1.7	Method 7: Sulfonation of 9H-Carbazole	728
10.15.4.2.1.8	Method 8: Nitration of 9H-Carbazole	729
10.15.4.2.1.9	Method 9: N-Metalation of 9H-Carbazole	729
10.15.4.2.1.10	Method 10: Substitution by Carbon Functionality at NH	729
10.15.4.2.1.10.1	Variation 1: Synthesis of 9-Acetylcarbazole	729
10.15.4.2.1.10.2	Variation 2: Microwave-Irradiation-Accelerated N-Alkylation	730
10.15.4.2.1.10.3	Variation 3: N-Alkylation with Dimethyl Sulfate	730
10.15.4.2.1.11	Method 11: N-Sulfonylation with Benzenesulfonyl Chloride	731
10.15.4.2.1.12	Method 12: N-Nitrosation of 9H-Carbazole	731
10.15.4.2.2	Substitution of Metals	732
10.15.4.2.2.1	Method 1: Silylation of (9-Ethylcarbazol-3-yl)lithium	732
10.15.4.2.3	Substitution of Carbon	732
10.15.4.2.3.1	Method 1: Decarboxylation with Copper and Quinoline	733
10.15.4.2.3.2	Method 2: Decarbonylation of Carbazolecarbaldehydes	733

10.15.4.2.3.3	Method 3: Dealkylation of <i>tert</i> -Butylcarbazoles	733
10.15.4.2.4	Substitution of Heteroatoms	734
10.15.4.2.4.1	Substitution by Hydrogen	734
10.15.4.2.4.1.1	Method 1: Reductive Removal of Sulfur	734
10.15.4.2.4.1.2	Method 2: Hydrolysis of 9-(Phenylsulfonyl)carbazoles	735
10.15.4.2.4.2	Substitution by Carbon Nucleophiles	735
10.15.4.2.4.2.1	Method 1: Suzuki Reaction of 1-Hydroxycarbazole Trifluoromethanesulfonate	735
10.15.4.2.4.2.2	Method 2: Displacement of Iodide with Copper(I) Cyanide	735
10.15.4.2.4.3	Substitution by Other Heteroatoms	736
10.15.4.2.4.3.1	Method 1: Replacement of a Diazonium Group by Chlorine (Sandmeyer Reaction)	736
10.15.4.2.4.3.2	Method 2: Nucleophilic Displacement of Bromine with Phenylhydrazine	736
10.15.4.3	Modification of Substituents	737
10.15.4.3.1	Method 1: Reduction of Aldehydes	737
10.15.4.3.2	Method 2: Reduction of Carbazolyl Ketones	738
10.15.4.3.3	Method 3: Trimethylsiloxy Cyanohydrin Formation from Ketones	738
10.15.4.3.4	Method 4: Reductive Hydrolysis of Trimethylsilyl Cyanohydrins	739
10.15.4.4	Rearrangement of Substituents	739
10.15.4.4.1	Method 1: Rearrangement of 9-(Phenylacetyl)carbazole	739
10.15.4.4.2	Method 2: Acetamidocarbazoles from Beckmann Rearrangement	740
10.16	Product Class 16: Indolizines M. Shipman	
10.16	Product Class 16: Indolizines	745
10.16.1	Synthesis by Ring-Closure Reactions	747
10.16.1.1	By Formation of One N—C and One C—C Bond	748
10.16.1.1.1	With Formation of 1—2 and 3—4 Bonds	748
10.16.1.1.1.1	Method 1: From 2-Ethynylpyridines and Acetylenes	748
10.16.1.1.1.2	Method 2: From 2-Substituted Pyridines and Alkenes	748
10.16.1.1.1.3	Method 3: From 2-Methylpyridines and Acid Anhydrides (Scholtz Reaction)	749
10.16.1.1.2	With Formation of 1—8a and 3—4 Bonds	750
10.16.1.1.2.1	Method 1: Palladium-Catalyzed Coupling Reactions of 2-Bromopyridines	750
10.16.1.1.2.2	Method 2: From Pyridines and Acetylenes	751
10.16.1.1.2.3	Method 3: From Pyridines and Cyclopropene Derivatives	751

10.16.1.1.3	With Formation of 2–3 and 3–4 Bonds	752
10.16.1.1.3.1	Method 1: From 2-Vinylpyridines and Carbenes	752
10.16.1.1.4	With Formation of 4–5 and 8–8a Bonds	753
10.16.1.1.4.1	Method 1: Condensation of Pyrrole with Hexane-2,5-dione	753
10.16.1.2	By Formation of Two C–C Bonds	754
10.16.1.2.1	With Formation of 1–8a and 2–3 Bonds	754
10.16.1.2.1.1	Method 1: 1,3-Dipolar Cycloadditions of Pyridinium Methylides	754
10.16.1.2.1.1.1	Variation 1: Pyridinium Methylides by Deprotonation	754
10.16.1.2.1.1.2	Variation 2: Pyridinium Methylides from Pyridines and Tetracyanoethylene Oxide	755
10.16.1.2.1.1.3	Variation 3: 1,3-Dipoles from 1-[(Trimethylsilyl)methyl]pyridinium Salts	756
10.16.1.2.1.1.4	Variation 4: 1,3-Dipoles from Carbenes	757
10.16.1.2.1.2	Method 2: From 2-Halopyridinium Salts and β -Dicarbonyl Compounds	758
10.16.1.3	By Formation of One N–C Bond	759
10.16.1.3.1	With Formation of the 3–4 Bond	759
10.16.1.3.1.1	Method 1: Cyclizations of 2-(Functionalized propyl)pyridine Derivatives	759
10.16.1.3.1.1.1	Variation 1: Oxidative Cyclizations of 3-(2-Pyridyl)propan-1-ols	759
10.16.1.3.1.1.2	Variation 2: Cyclizations of 3-(2-Pyridyl)propanediols and Their Derivatives	760
10.16.1.3.1.1.3	Variation 3: Cyclizations of 1-(2-Pyridyl)prop-2-en-1-ols and Their Derivatives	760
10.16.1.3.1.1.4	Variation 4: Cyclizations of 3-(2-Pyridylmethylene)pentane-2,4-diones	762
10.16.1.3.1.1.5	Variation 5: Cyclizations of 3-(2-Pyridyl)propanals and Their Derivatives	762
10.16.1.3.1.2	Method 2: Thermal Rearrangement of 2-(Buten-3-ynyl)pyridine <i>N</i> -Oxides	763
10.16.1.3.2	With Formation of the 4–5 Bond	764
10.16.1.3.2.1	Method 1: Indolizine-8-carbonitriles by Ring-Closure Reactions of Pyrroles	764
10.16.1.3.2.2	Method 2: Indolizine-5,8-diones by Ring-Closure Reactions of Pyrroles	764
10.16.1.4	By Formation of One C–C Bond	765
10.16.1.4.1	With Formation of the 1–2 Bond	765
10.16.1.4.1.1	Method 1: Tschitschibabin Reaction	765
10.16.1.4.1.1.1	Variation 1: Base-Induced Cyclizations of Pyridinium Salts	766
10.16.1.4.1.1.2	Variation 2: One-Pot Tschitschibabin Reactions	767
10.16.1.4.1.2	Method 2: Synthesis of Indolizin-2(3 <i>H</i>)-ones	768
10.16.1.4.1.3	Method 3: Indolizines from Pirylium Salts	768
10.16.1.4.1.4	Method 4: 1,2-Disubstituted Indolizines from 2-Acyl- <i>N</i> -(acylmethyl)pyridinium Salts	769
10.16.1.4.2	With Formation of the 1–8a Bond	770
10.16.1.4.2.1	Method 1: 1,5-Dipolar Cyclizations of <i>N</i> -Allylpyridinium Salts	770
10.16.1.4.2.2	Method 2: Synthesis of 2,3-Benzindolizines	770

10.16.1.4.3	With Formation of the 2–3 Bond	771
10.16.1.4.3.1	Method 1: Cyclizations of 2-Ethynylpyridinium Salts	771
10.16.1.4.3.2	Method 2: Cyclization Reactions of 2-Methylene-1,2-dihydropyridines	772
10.16.1.4.3.2.1	Variation 1: Cyclizations of 2-Methylene- and 2-Allylidene-1,2-dihydropyridines	772
10.16.1.4.3.2.2	Variation 2: Metalation/Ring Closure of 2-(Benzoylmethylene)-1,2-dihydropyridines	773
10.16.1.4.4	With Formation of the 8–8a Bond	774
10.16.1.4.4.1	Method 1: Indolizine-5,8-diones from 4-(1 <i>H</i> -Pyrrol-1-yl)cyclobutenones	774
10.16.2	Synthesis by Ring Transformation	775
10.16.2.1	Method 1: Ring Contraction of 4 <i>H</i> -Quinolizines	775
10.16.2.2	Method 2: Ring Contraction of Dihydropyridothiazines	776
10.16.2.3	Method 3: Ring Expansion of 3 <i>H</i> -Pyrrolizine	776
10.16.3	Synthesis by Substituent Modification	777
10.16.3.1	Substitution of Existing Substituents	777
10.16.3.1.1	Of Hydrogen	777
10.16.3.1.1.1	Method 1: Deuteration of Indolizines	777
10.16.3.1.1.2	Method 2: Lithiation of Indolizines	777
10.16.3.1.1.3	Method 3: Introduction of Carbon Substituents	778
10.16.3.1.1.4	Method 4: Introduction of Nitrogen Substituents	779
10.16.3.1.1.5	Method 5: Introduction of Sulfur Substituents	780
10.16.3.1.2	Of Metals	781
10.16.3.1.2.1	Method 1: Substitution Reactions of 5-Lithioindolizines	781
10.16.3.1.2.2	Method 2: Protodesilylation of Trimethylsilyl-Substituted Indolizines	781
10.16.3.1.3	Of Carbon Functionalities	782
10.16.3.1.3.1	Method 1: By Cleavage of C–C Bonds	782
10.16.3.2	Modification of α -Carbon Substituents	783
10.16.3.2.1	Method 1: By Manipulations at the α -Carbon Atom	783
10.17	Product Class 17: Benzo[<i>b</i>]phospholes R. A. Aitken	
10.17	Product Class 17: Benzo[<i>b</i>]phospholes	789
10.17.1	Synthesis by Ring-Closure Reactions	790
10.17.1.1	By Annulation to an Arene	790
10.17.1.1.1	By Formation of Two P–C Bonds	790
10.17.1.1.1.1	Method 1: Reaction of Lithiated Phenylalkyne Derivatives with Phosphorus Dihalides	790
10.17.1.1.1.2	Method 2: Reaction of a Zirconacycle with Phosphorus Dihalides	791

10.17.1.1.1.3	Method 3: Reaction of Phenylalkynes with Phosphorus Pentachloride ...	791
10.17.1.1.2	By Formation of One P—C Bond	792
10.17.1.1.2.1	Method 1: Base-Induced Cyclization of 2-Alkynylphenylphosphines	792
10.17.1.1.2.2	Method 2: Photochemical Cyclization of a 2-Alkynylphenylphosphine ...	793
10.17.1.1.2.3	Method 3: Thermal Cyclization of 2-(Phenylalkynyl)phenylchlorophosphines	794
10.17.1.2	By Annulation to a Phosphole	796
10.17.1.2.1	Method 1: Sulfurization of a Phosphole [2 + 2] Dimer	796
10.17.1.2.2	Method 2: Thermolysis of a Phosphole [4 + 2] Dimer	796
10.17.2	Synthesis by Ring Transformation	797
10.17.2.1	Method 1: Photochemical Rearrangement of a Phosphadiazole	797
10.17.3	Aromatization	798
10.17.3.1	By Aromatization of 2,3-Dihydrobenzo[<i>b</i>]phospholes	798
10.17.3.1.1	Method 1: Dehydrobromination	798
10.17.3.1.1.1	Variation 1: Using Triethylamine	798
10.17.3.1.1.2	Variation 2: Using 1,8-Diazabicyclo[5.4.0]undec-7-ene	799
10.17.3.1.2	Method 2: Gas-Phase Dehydrochlorination over a Solid Base	800
10.17.3.1.3	Method 3: Deprotonation of a Cyclic Phosphonium Salt	801
10.17.4	Synthesis by Substituent Modification	801
10.17.4.1	Modification at Phosphorus	802
10.17.4.1.1	Addition Reactions	802
10.17.4.1.1.1	Method 1: Oxidation	802
10.17.4.1.1.2	Method 2: Formation of an Ylide	802
10.17.4.1.2	Substitution Reactions	803
10.17.4.1.2.1	Method 1: Substitution of Halogen	803
10.17.4.1.2.2	Method 2: Substitution of Aryl Groups	804
10.17.4.1.3	Reduction	805
10.17.4.1.3.1	Method 1: Reduction of <i>P</i> -Oxides	805
10.17.4.2	Modification at Carbon	805
10.17.4.2.1	Substitution Reactions	805
10.17.4.2.1.1	Method 1: Removal of Silyl Groups	805
10.17.4.2.1.2	Method 2: Halogenation	805
10.17.4.3	Modification of Substituents	806
10.17.4.3.1	Method 1: Reaction of a 2,3-Dihydrobenzo[<i>b</i>]phosphol-3-one with Electrophiles	806

10.18	Product Class 18: Benzo[c]phospholes R. A. Aitken	
<hr/>		
10.18	Product Class 18: Benzo[c]phospholes	809
10.18.1	Synthesis by Ring-Closure Reactions	809
10.18.1.1	By Annulation to a Benzene Ring	809
10.18.1.1.1	By Formation of Two P—C Bonds	809
10.18.1.1.1.1	Method 1: From Phthaloyl Chloride	810
10.18.1.1.1.2	Method 2: From a Bis(phosphonium salt)	810
10.18.2	Aromatization	811
10.18.2.1	Of a 1,3-Dihydrobenzo[c]phosphole	811
10.18.2.1.1	Method 1: Formation of 1 <i>H</i> -Benzo[c]phospholes	812
10.18.2.1.2	Method 2: Formation of 2 <i>H</i> -Benzo[c]phospholes	812
10.19	Product Class 19: Dibenzophospholes R. A. Aitken	
<hr/>		
10.19	Product Class 19: Dibenzophospholes	817
10.19.1	Synthesis by Ring-Closure Reactions	818
10.19.1.1	By Annulation to an Arene	819
10.19.1.1.1	By Formation of Two P—C Bonds	819
10.19.1.1.1.1	Method 1: Reaction of 2,2'-Dilithiobiaryls with Phosphorus Trihalides ...	819
10.19.1.1.1.2	Method 2: Reaction of 2,2'-Dilithiobiaryls with Phosphinimines	820
10.19.1.1.1.3	Method 3: Reaction of 2,2'-Dilithiobiphenyl with Phosphorus Pentachloride	821
10.19.1.1.1.4	Method 4: Reaction of 2,2'-Biphenylenemercury with a Phosphinine ...	821
10.19.1.1.1.5	Method 5: Reaction of Biphenylene with Phenylphosphinidene	822
10.19.1.1.2	By Formation of One P—C Bond	822
10.19.1.1.2.1	Method 1: From Biphenyl-2-yl-dichlorophosphine	822
10.19.1.1.2.2	Method 2: From Biphenyl-2-yl-metaphosphonate	822
10.19.1.1.2.3	Method 3: From Biphenyl-2-yl-oxy-dichlorophosphine	823
10.19.1.1.2.4	Method 4: From Biphenyl-2-yl-phosphinic Acids	824
10.19.1.1.2.5	Method 5: From Biphenylene-2,2'-bis(phosphonium salts)	824
10.19.1.1.3	By Formation of One C—C Bond	825
10.19.1.1.3.1	Method 1: Palladium-Catalyzed Cyclization of Bis(2-haloaryl)phosphinic Acids	825
10.19.1.1.3.2	Method 2: Reaction of Triphenylphosphonium Salts and Other Triphenylphosphorus Compounds with Strong Bases ..	825
10.19.2	Aromatization	827
10.19.2.1	Method 1: Of Decahydrodibenzophospholes from the McCormack Reaction	827

10.19.3	Synthesis by Substituent Modification	828
10.19.3.1	Modification at Phosphorus	828
10.19.3.1.1	Addition Reactions	828
10.19.3.1.1.1	Method 1: Addition of Hydride and Carbanions to Phosphonium Salts	828
10.19.3.1.1.2	Method 2: P-Alkylation	829
10.19.3.1.1.3	Method 3: Formation of <i>P</i> -Oxides, -Sulfides, and -Selenides	830
10.19.3.1.1.4	Method 4: Formation of <i>P</i> -N Compounds	831
10.19.3.1.2	Substitution Reactions	831
10.19.3.1.2.1	Method 1: Replacement of <i>P</i> -Alkyl or -Phenyl Groups by Other Alkyls ...	831
10.19.3.1.2.2	Method 2: Replacement of <i>P</i> -Alkyl or -Phenyl Groups by Hydroxide	832
10.19.3.1.2.3	Method 3: Reduction of <i>P</i> -Chloro Compounds	833
10.19.3.1.2.4	Method 4: Reaction of <i>P</i> -Chloro Compounds with Grignard Reagents ...	833
10.19.3.1.2.5	Method 5: Use of <i>P</i> -Halo Compounds To Form Phosphoranes	834
10.19.3.1.2.6	Method 6: Reduction of <i>P</i> -Oxides	834
10.19.3.1.2.7	Method 7: Conversion of <i>P</i> -Selenides into <i>P</i> -Oxides	835
10.19.3.1.3	Reductive Elimination	835
10.19.3.1.3.1	Method 1: Reductive Elimination at Phosphorus	835
10.20	Product Class 20: Phosphorus Analogues of Indolizines R. A. Aitken	
<hr/>		
10.20	Product Class 20: Phosphorus Analogues of Indolizines	839
10.20.1	Annulation to a Phosphole	839
10.20.1.1	Method 1: Cycloaddition of Phospholes with Dimethyl Acetylenedicarboxylate	839
	Keyword Index	843
	Author Index	861
	Abbreviations	911