

 WILEY

CATALYSTS FOR FINE CHEMICAL SYNTHESIS

Metal Catalysed
Carbon-Carbon
Bond-Forming Reactions

3

Editors: Stanley M. Roberts, Jianliang Xiao,
John Whittall and Tom E. Pickett

Contents

Series Preface	xvii
Preface to Volume 3	xix
Abbreviations	xxi
List of Chemical Names Used	xxiii
1 Considerations of Industrial Fine Chemical Synthesis	1
<i>Mark W. Hooper</i>	1
1.1 Introduction	
1.2 Types of processes – flow charts	2
1.2.1 Classical process	2
1.2.2 General catalytic process	3
1.3 Costs associated with use of catalysts	3
1.3.1 Catalyst fabrication costs	3
1.3.2 Intellectual property right (IPR) issues	6
1.3.3 Separation costs	7
1.3.4 Pre-reaction/immobilisation	7
1.3.5 Post reaction – separation	8
1.3.6 Industrial examples	9
References	12
2 Alkylation and Allylation Adjacent to a Carbonyl Group	13
2.1 The $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ -catalysed alkylation, alkenylation and arylation of aromatic ketones via carbon-hydrogen bond cleavage <i>Fumitoshi Kakiuchi, Satoshi Ueno and Naoto Chatani</i>	14
2.1.1 Preparation of carbonyldihydrotris(triphenylphosphine) ruthenium	14
2.1.2 Synthesis of 8-(2-triethoxysilanylethyl)-3,4-dihydro-2H- naphthalen-1-one	16
2.1.3 Synthesis of 8-(1-methyl-2-trimethylsilylvinyl)-3,4- dihydro-2H-naphthalen-1-one	17
2.1.4 Synthesis of 1-biphenyl-2-yl-2,2-dimethylpropan-1-one	18

2.1.5	Conclusion	19
	References	21
2.2	Catalytic, asymmetric synthesis of α,α -disubstituted amino acids using a chiral copper-salen complex as a phase transfer catalyst <i>Michael North and Jose A. Fuentes</i>	21
2.2.1	Synthesis of (chsalen)	22
2.2.2	Synthesis of copper(II) (chsalen).	23
2.2.3	Alkylation of alanine methyl ester Schiff base by chiral salen-metal catalysts, α -benzyl-alanine methyl ester	24
2.2.4	Conclusion	26
	References	27
2.3	Asymmetric phase-transfer catalysed alkylation of glycine imines using cinchona alkaloid derived quaternary ammonium salts <i>Barry Lygo and Benjamin I. Andrews</i>	27
2.3.1	Synthesis of (1 <i>S</i> ,2 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,1' <i>R</i>)-1-(anthracen-9-ylmethyl)-5-ethyl-2-[hydroxy(quinolin-4-yl)methyl]-1-azoniabicyclo[2.2.2]octane bromide	28
2.3.2	Synthesis of (1 <i>S</i> ,2 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,1' <i>R</i>)-1-(anthracen-9-ylmethyl)-5-ethyl-2-[benzyloxy(quinolin-4-yl)methyl]-1-azoniabicyclo[2.2.2]octane bromide	29
2.3.3	Synthesis of (2 <i>S</i>)-tert-butyl 2-amino-4-bromopent-4-enoate	31
2.3.4	Conclusion	32
	References	33
3	Asymmetric Alkylation or Amination of Allylic Esters	35
3.1	Synthesis and application in palladium-catalysed asymmetric allylic substitution of enantiopure cyclic β -iminophosphine ligands <i>Maria Zablocka, Marek Koprowski, Jean-Pierre Majoral, Mathieu Achard and Gérard Buono</i>	36
3.1.1	Synthesis of (2,6-dimethyl-phenyl)-(1-phenyl-2,3,3a,8a-tetrahydro-1H-1-phospha-cyclopenta[α]inden-8-ylidene)-amines 1 <i>R_p</i>	36
3.1.2	Synthesis of (<i>E</i>)-Methyl 2-carbomethoxy-3,5-diphenylpent-4-enoate	37
3.1.3	Synthesis of benzyl(1,3-diphenylprop-2-enyl)amine	39
3.1.4	Conclusion	40
	References	40
3.2	(9H,9' <i>H</i> ,10H,10' <i>H</i> ,11H,11 <i>H'</i> ,13H,13' <i>H</i> ,14H,14' <i>H</i> ,15H,15' <i>H</i> -perfluorotricosane-12,12'-diyl)bis[(4 <i>S</i>)-4-phenyl-2-oxazoline as a ligand for asymmetric palladium-catalysed alkylation of allylic acetates in fluorous media <i>Jérôme Bayardon and Denis Sinou</i>	40

3.2.1	Synthesis of 2-iodo-1-(1H,1'H,2H,2'H,3H,3'H-perfluorooctyl)-3-propanol	41
3.2.2	Synthesis of 3-(1H,1'H,2H,2'H,3H,3'H-perfluorooctyl)-1-propanol	42
3.2.3	Synthesis of 3-(1H,1'H,2H,2'H,3H,3'H-perfluorooctyl)-1-iodopropane	43
3.2.4	Synthesis of (9H,9'H,10H,10'H,11H,11'H,13H,13'H,14H,14'H,15H,15'H-perfluorotricosane-12,12'-diyl)-bis-[(4 <i>S</i>)-4-phenyl-2-oxazoline]	44
3.2.5	Synthesis of (<i>E</i>)-Methyl 2-carbomethoxy-3,5-diphenylpent-4-enoate	45
3.2.6	Conclusion	46
	References	47
3.3	Facile synthesis of new axially chiral diphosphine complexes for asymmetric catalysis <i>Matthias Lotz, Gernot Kramer, Katja Tappe and Paul Knochel</i>	47
3.3.1	Synthesis of (<i>S</i> _{FC})-1-[(<i>S</i>)- <i>p</i> -tolylsulfinyl]-2-[(<i>o</i> -diphenylphosphino)phenyl]ferrocene	47
3.3.2	Synthesis of (<i>S</i> _{FC})-1-diphenylphosphino-2-[(<i>o</i> -diphenylphosphino)phenyl]ferrocene	49
3.3.3	Conclusion	50
	References	51
3.4	Chiral ferrocenyl-imino phosphines as ligands for palladium-catalysed enantioselective allylic alkylations <i>Pierluigi Barbaro, Claudio Bianchini, Giuliano Giambastiani and Antonio Togni</i>	51
3.4.1	Synthesis of the precursor (<i>R</i>)-1-[(<i>S</i>)-2-bromoferrocenyl]ethyl-diphenylphosphine	52
3.4.2	Synthesis of key precursor (<i>R</i>)-1-[(<i>S</i>)-2-formylferrocenyl]ethyl-diphenylphosphine	53
3.4.3	Synthesis of (<i>R</i>)-1-[(<i>S</i>)-2-ferrocenylidene-ethyl-imine]ethyl-diphenylphosphine	54
3.4.4	Conclusion	55
	References	56
4	Suzuki Coupling Reactions	59
4.1	Palladium-catalysed borylation and Suzuki coupling (BSC) to obtain β -benzo[<i>b</i>]thienyldehydroamino acid derivatives <i>Ana S. Abreu, Paula M. T. Ferreira and Maria-João R. P. Queiroz</i>	60
4.1.1	Synthesis of the <i>E</i> and <i>Z</i> isomers of the methyl ester of <i>N</i> -tert-butoxycarbonyl- β -bromodehydroaminobutyric acid	61
4.1.2	Synthesis of the methyl ester of <i>N</i> -tert-butoxycarbonyl-(<i>Z</i>)-[β -(2,3,7-trimethylbenzo[<i>b</i>]thien-6-yl)]dehydroaminobutyric acid	62

4.1.3	Conclusion	64
	References	64
4.2	Palladium-catalysed cross-coupling reactions of 4-tosylcoumarins and arylboronic acids: synthesis of 4-arylcoumarin compounds <i>Jie Wu, Lisha Wang, Reza Fathi and Zhen Yang</i>	64
4.2.1	Synthesis of 4-tosylcoumarins	65
4.2.2	Synthesis of 4-arylcoumarin	65
4.2.3	Conclusion	66
	References	66
4.3	Cyclopropyl arenes, alkynes and alkenes from the <i>in situ</i> generation of B-cyclopropyl-9-BBN and the Suzuki-Miyaura coupling of aryl, alkynyl and alkenyl bromides <i>Ramon E. Huertas and John A. Soderquist</i>	67
4.3.1	Synthesis of 4-cyclopropylbenzaldehyde	67
4.3.2	Conclusion	69
	References	69
4.4	One-pot synthesis of unsymmetrical 1,3-dienes through palladium-catalysed sequential borylation of a vinyl electrophile by a diboron and cross-coupling with a distinct vinyl electrophile <i>Tatsuo Ishiyama and Norio Miyaura</i>	70
4.4.1	Synthesis of 2-(1-cyclopentenyl)-1-decene	70
4.4.2	Conclusion	73
	References	74
4.5	Pd(OAc) ₂ /2-Aryl oxazoline catalysed Suzuki coupling reactions of aryl bromides and boronic acids <i>Bin Tao and David W. Boykin</i>	74
4.5.1	Synthesis of 4-methoxybiphenyl	75
4.5.2	Conclusion	76
	References	77
4.6	Palladium-catalysed reactions of haloaryl phosphine oxides: modular routes to functionalised ligands <i>Colin Baillie, Lijin Xu and Jianliang Xiao</i>	77
4.6.1	Synthesis of 2-diphenylphosphinyl-2'-methoxybiphenyl via Suzuki coupling	78
4.6.2	Synthesis of 2-diphenylphosphino-2'-methoxybiphenyl	79
4.6.3	Conclusion	80
	References	80
4.7	Bulky electron rich phosphino-amines as ligands for the Suzuki coupling reaction of aryl chlorides <i>Matthew L. Clarke and J. Derek Woollins</i>	81
4.7.1	Synthesis of N-di-isopropylphosphino-N-methyl piperazine	82

4.7.2	Suzuki coupling reactions using isolated ligand and Pd ₂ dba ₃ .CHCl ₃ as catalyst	83
4.7.3	<i>In situ</i> ligand preparation and application in Suzuki coupling of 3-fluorobenzene with phenylboronic acid . . .	84
4.7.4	Conclusion	85
	References	85
4.8	Arylation of ketones, aryl amination and Suzuki-Miyaura cross coupling using a well-defined palladium catalyst bearing an <i>N</i> -heterocyclic carbene ligand <i>Nicholas Marion, Oscar Navarro, Roy A. Kelly III and Steven P. Nolan</i>	86
4.8.1	Synthesis of 1,2-diphenyl-ethanone by ketone arylation	86
4.8.2	Synthesis of dibutyl- <i>p</i> -tolyl-amine by aryl amination . . .	88
4.8.3	Synthesis of 4-methoxybiphenyl	89
4.8.4	Conclusion	90
	References	90
5	Heck Coupling Reactions	91
5.1	Palladium-catalysed multiple and asymmetric arylations of vinyl ethers carrying co-ordinating nitrogen auxiliaries: synthesis of arylated ketones and aldehydes <i>Peter Nilsson and Mats Larhed</i>	92
5.1.1	Triarylation: synthesis of <i>N,N</i> -dimethyl-2-[1,2,2-(triaryl)ethenyloxy]ethanamines with subsequent hydrolysis furnishing 1,2,2-triaryl ethanones, Table 5.1	92
5.1.2	Terminal diarylation: synthesis of <i>N,N</i> -dimethyl-2-[2,2-diarylethenyloxy]ethanamine with subsequent hydrolysis furnishing diaryl ethanals Table 5.2	95
5.1.3	Asymmetric Heck arylation: synthesis of 2-aryl-2-methylcyclopentanone	97
	Conclusion	99
	References	99
5.2	Palladium-catalysed highly regioselective arylation of electron-rich olefins <i>Lijin Xu, Jun Mo and Jianliang Xiao</i>	100
5.2.1	Synthesis of 1-acetonaphthone	100
5.2.2	Synthesis of 3-acetylbenzonitrile	102
	Conclusion	104
	References	104
5.3	1-[4-(<i>S</i>)- <i>tert</i> -Butyl-2-oxazolin-2-yl]-2-(<i>S</i>)-(diphenylphosphino)ferrocene as a ligand for the palladium-catalysed intermolecular asymmetric Heck reaction of 2,3-dihydrofuran <i>Tim G. Kilroy, Yvonne M. Malone and Patrick J. Guiry</i>	104

5.3.1	Synthesis of <i>N</i> -[1-(<i>S</i>)-(Hydroxymethyl)-2,2-dimethyl-propyl]ferrocenecarboxamide	106
5.3.2	Synthesis of [4-(<i>S</i>)- <i>tert</i> -butyl-2-oxazolin-2-yl]ferrocene	107
5.3.3	Synthesis of 1-[4-(<i>S</i>)- <i>tert</i> -butyl-2-oxazolin-2-yl]-2-(<i>S</i>)-(diphenylphosphino)ferrocene	108
5.3.4	Asymmetric phenylation of 2,3-dihydrofuran	110
	Conclusion	112
	References	112
6	Sonogashira Coupling Reactions	113
6.1	Nonpolar biphasic catalysis: Suzuki- and Sonogashira coupling reactions <i>Anupama Datta and Herbert Plenio</i>	113
6.1.1	Nonpolar biphasic Sonogashira reaction of 4-bromoacetophenone and phenylacetylene to 1-(4-phenylethynyl-phenyl)-ethanone	114
6.1.2	Nonpolar biphasic Suzuki reaction for the synthesis of 1-biphenyl-4-yl-ethanone	115
	Conclusion	116
	References	116
6.2	Polystyrene-supported soluble palladacycle catalyst as recyclable catalyst for Heck, Suzuki and Sonogashira reactions <i>Chih-An Lin and Fen-Tair Luo</i>	116
6.2.1	Synthesis of 3-bromo-4-methylacetophenone	117
6.2.2	Synthesis of 1-(3-bromo-4-methyl-phenyl)-ethanol	118
6.2.3	Synthesis of 3-bromo-4-methyl-styrene	120
6.2.4	Synthesis of 3-(diphenylphosphino)-4-methyl-styrene	121
6.2.5	Synthesis of <i>trans</i> -di(μ -acetato)-bis[3-(diphenylphosphino)-4-styryl]dipalladium(II)	122
6.2.6	Synthesis of polymer-supported palladacycle catalyst	123
6.2.7	Synthesis of 1-[4-(2-phenylethynyl)phenyl]ethan-1-one <i>via</i> Sonogashira reaction by the use of polymer-supported palladacycle catalyst	124
	Conclusion	125
	Reference	125
7	Cross-Coupling Reactions	127
7.1	Cross-coupling reaction of alkyl halides with Grignard reagents in the presence of 1,3-butadiene catalysed by nickel, palladium, or copper <i>Jun Terao and Nobuaki Kambe</i>	128
7.1.1	Synthesis of nonylcyclopropane	128
7.1.2	Synthesis of 4-bromo-hexylbenzene	130
7.1.3	Synthesis of 1,1-diphenyl-1-nonene	131

Conclusion	132
References	132
7.2 Triorganoindium compounds as efficient reagents for palladium-catalysed cross-coupling reactions with aryl and vinyl electrophiles	
<i>Luis A. Sarandeses and José Pérez Sestelo</i>	133
7.2.1 Preparation of triphenylindium	134
7.2.2 Synthesis of 4-acetylbiphenyl	134
7.2.3 Synthesis of 1,3-diphenyl-2-propen-1-one	136
Conclusion	137
References	138
7.3 Cross-coupling reactions catalysed by heterogeneous nickel-on-charcoal	
<i>Bryan A. Frieman and Bruce H. Lipshutz</i>	138
7.3.1 Preparation of the heterogeneous catalyst: nickel-on-charcoal	139
7.3.2 Ni/C-catalysed Suzuki couplings: 2-cyanobiphenyl	140
7.3.3 Ni/C-catalysed aromatic aminations: <i>N</i> -(4-cyanophenyl)-morpholine	141
7.3.4 Ni/C-catalysed cross-couplings <i>en route</i> to allylated aromatics: toluene-4-sulfonic acid 2-(3,7,11,15,19,23,27,31,35,39-decamethyltetraconta-2,6,10,14,18,22,26,-30,34,38-decaenyl)-5,6-dimethoxy-3-methylphenyl ester (coenzyme Q ₁₀ precursor)	142
7.3.5 Ni/C-catalysed reductions of aryl chlorides	144
7.3.6 Microwave assisted Ni/C-catalysed cross coupling of vinyl zirconocenes and aryl halides: 1-octenyl-4-trifluoromethylbenzene	145
Conclusion	147
References	147
7.4 Carbon-carbon bond formation using arylboron reagents with rhodium(I) catalysts in aqueous media	
<i>John Mancuso, Masahiro Yoshida and Mark Lautens</i>	147
7.4.1 Synthesis of (<i>E</i>)-2-[2-(2-methylphenyl)-1-hexenyl]pyridine	148
7.4.2 Synthesis of methyl (2 <i>EZ</i>)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]acrylate	149
7.4.3 Synthesis of methyl (1 <i>S</i> *,4 <i>R</i> *,4 <i>aS</i> *,9 <i>S</i> *,9 <i>aS</i> *)-2,3,4,4 <i>a</i> ,9,9 <i>a</i> -hexahydro-1 <i>H</i> -1,4-methano-fluoren-9-ylacetate	151
References	153
8 Regioselective or Asymmetric 1,2-Addition to Aldehydes	155
8.1 Development of a highly regioselective metal-mediated allylation reaction in aqueous media	
<i>Kui-Thong Tan, Shu-Sin Chng, Hin-Soon Cheng and Teck-Peng Loh</i>	156

8.1.1	Synthesis of 1-cyclohexylpent-3-en-1-ol using indium-mediated allylation	156
8.1.2	Synthesis of 1-cyclohexylpent-3-en-1-ol using tin-mediated allylation	157
8.1.3	Synthesis of 1-cyclohexylpent-3-en-1-ol using zinc-mediated allylation	159
	Conclusion	160
	References	161
8.2	Boronic acids as aryl source for the catalysed enantioselective aryl transfer to aldehydes <i>Jens Rudolph and Carsten Bolm</i>	161
8.2.1	Preparation of (<i>S</i>)-4-tolyl-phenyl methanol	161
	Conclusion	163
	References	163
8.3	Jacobsen's Salen as a chiral ligand for the chromium-catalysed addition of 3-chloro-propenyl pivalate to aldehydes: a catalytic asymmetric entry to syn-alk-1-ene-3,4-diols <i>Marco Lombardo, Sebastiano Licciulli, Stefano Morganti and Claudio Trombini</i>	164
8.3.1	Synthesis of 3-chloro-propenyl pivalate	165
8.3.2	Synthesis of alk-1-ene-3,4-diols: Salen-Cr(II) catalysed addition of 3-chloro-propenyl pivalate to cyclohexanecarboxaldehyde	166
	Conclusion	168
	References	168
9	Olefin Metathesis Reactions	169
9.1	Highly active ruthenium (pre)catalysts for metathesis reactions <i>Syuzanna Harutyunyan, Anna Michrowska and Karol Grela</i>	169
9.1.1	Synthesis of the ruthenium (pre)catalyst	170
9.1.2	Synthesis of 1-[(4-methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1H-azepine	171
	Conclusion	172
	References	173
9.2	A highly active and readily recyclable olefin metathesis catalyst <i>Stephen J. Connon, Aideen M. Dunne and Siegfried Blechert</i>	174
9.2.1	Synthesis of polymer supported catalyst (3)	174
9.2.2	Ring-closing metathesis of an acyclic diene and subsequent catalyst recovery/reuse	176
	Conclusion	177
	References	177
9.3	Stereoselective synthesis of L-733,060 <i>G. Bhaskar and B. Venkateswara Rao</i>	178

9.3.1	Synthesis of (2 <i>S</i> ,3 <i>S</i>)- <i>N</i> -tert-butoxycarbonyl-2-phenyl 1,2,3,6-tetrahydro-3-pyridinol	179
	Conclusion	180
	References	180
10	Cyclisation Reactions	181
10.1	Molecular sieves as promoters for the catalytic Pauson-Khand reaction <i>Jaime Blanco-Urgoiti, Gema Domínguez and Javier Pérez-Castells</i>	182
10.1.1	Synthesis of 3 <i>aS</i> *,5 <i>R</i> *-5-hydroxy-3,3 <i>a</i> ,4,5- tetrahydrocyclopenta[<i>a</i>]naphthalen-2-one	182
	Conclusion	185
	References	185
10.2	Palladium(II)-catalysed cyclization of alkynes with aldehydes, ketones or nitriles initiated by acetoxypalladation of alkynes <i>Ligang Zhao and Xiyang Lu</i>	185
10.2.1	Synthesis of 3-phenyl-3-hydroxy-4-(1'-acetoxy- hexylidene)tetrahydrofuran	186
10.2.2	Synthesis of dimethyl 3-acetylamino-4-butyrylcyclo- pent-3-ene-1,1-dicarboxylate	187
	Conclusion	188
	References	190
10.3	Rhodium(I)-catalysed intramolecular alder-ene reaction and syntheses of functionalised α -methylene- γ -butyrolactones and cyclopentanones <i>Minsheng He, Aiwen Lei and Xumu Zhang</i>	190
10.3.1	Synthesis of (4-benzylidene-5-oxo-tetrahydro-furan- 3-yl)-acetaldehyde	190
10.3.2	Synthesis of (3-oxo-2-pentylidene-cyclopentyl)- acetaldehyde	191
	References	192
10.4	Rhodium-catalysed [2 + 2 + 2] cyclootrimerisation in an aqueous-organic biphasic system <i>Hiroshi Shinokubo and Koichiro Oshima</i>	193
10.4.1	<i>In situ</i> preparation of a water-soluble rhodium catalyst from [RhCl(COD)] ₂ and trisodium salt of tris(<i>m</i> -sulfonatophenyl)phosphine (tppts)	193
10.4.2	Synthesis of 1,3,6,8,9,10,11,12,13-nonahydro- 2,7-dioxacyclodeca[<i>e</i>]indene	194
	Conclusion	195
	References	196
10.5	Titanocene-catalysed transannular cyclisation of epoxygerm- acrolides: enantiospecific synthesis of eudesmanolides <i>Antonio Rosales, Juan M. Cuerva and J. Enrique Oltra</i>	196

10.5.1	Preparation and titanocene-catalysed cyclization of epoxygermacrolide: synthesis of (+)-11 β ,13-dihydroreynosin	197
10.5.2	Titanocene-catalysed cyclization of epoxygermacrolide in aqueous medium	198
	References	199
11	Asymmetric Aldol and Michael Reactions	201
11.1	Direct catalytic asymmetric aldol reaction of a α -hydroxyketone promoted by an Et ₂ Zn/linked-BINOL complex <i>Masakatsu Shibasaki, Shigeki Matsunaga and Naoya Kumagai</i>	202
11.1.1	Synthesis of (2 <i>R</i> ,3 <i>S</i>)-2,3-dihydroxy-1-(2-methoxyphenyl)-5-phenyl-1-pentanone by the first generation Et ₂ Zn/linked-BINOL = 2/1 complex	203
11.1.2	Synthesis of (2 <i>R</i> ,3 <i>S</i>)-3-cyclohexyl-2,3-dihydroxy-1-(2-methoxyphenyl)-1-propanone by the second generation Et ₂ Zn/linked-BINOL = 4/1 complex with MS3A	205
	Conclusion	207
	References	208
11.2	Highly enantioselective direct aldol reaction catalysed by a novel small organic molecule <i>Zhuo Tang, Liu-Zhu Gong, Ai-Qiao Mi and Yao-Zhong Jiang</i>	208
11.2.1	Synthesis of (<i>S,S,S</i>)-pyrrolidine-2-carboxylic acid (2'-hydroxyl-1',2'-diphenyl-ethyl)-amine (1)	208
11.2.2	Direct aldol reaction	209
	Reference	210
11.3	Direct catalytic asymmetric Michael reaction of α -hydroxyketone promoted by Et ₂ Zn/linked-BINOL complex <i>Masakatsu Shibasaki, Shigeki Matsunaga and Naoya Kumagai</i>	210
11.3.1	Synthesis of (2 <i>R</i>)-2-hydroxy-1-(2-methoxyphenyl)-1,5-hexanedione by the first generation Et ₂ Zn/linked-BINOL = 2/1 complex	211
11.3.2	Synthesis of (2 <i>R</i>)-2-hydroxy-1-(2-methoxyphenyl)-1,5-hexanedione by the second Et ₂ Zn/linked-BINOL = 4/1 complex with MS 3A	213
	Conclusion	215
	References	215
11.4	Catalytic enantioselective Michael reaction catalysed by well-defined chiral ruthenium-amido complexes <i>Masahito Watanabe, Kunihiko Murata, and Takao Ikariya</i>	216
11.4.1	Synthesis of Ru[(<i>R,R</i>)-Tsdpen](η^6 -arene); Ru[(<i>R,R</i>)-Tsdpen](<i>p</i> -cymene), ((<i>R,R</i>)-TsDPEN = (1 <i>R</i> ,2 <i>R</i>)- <i>N</i> -(<i>p</i> -toluenesulfonyl)-1,2-diphenylethylenediamine),	

	(<i>p</i> -cymene = η^6 -1-CH ₃ -4-CH(CH ₃) ₂ C ₆ H ₄) ^{8b} , Ru[(<i>R,R</i>)-Tsdpen](hmb), and Ru[(<i>R,R</i>)-Msdpen](hmb)	217
11.4.2	Synthesis of (<i>S</i>)-3-di(methoxycarbonyl)methyl-1-cyclopentanone from the Michael reaction of dimethyl malonate and 2-cyclopenten-1-one catalysed by Ru[(<i>R,R</i>)-Tsdpen](hmb)	219
11.4.3	Synthesis of (<i>S</i>)-3-di(methoxycarbonyl)methyl-1-cyclopentanone from the Michael reaction of dimethyl malonate and cyclopentenone catalyzed by Ru[(<i>R,R</i>)-N-Msdpen](hmb)	220
11.4.4	Synthesis (<i>S</i>)-3-di(methoxycarbonyl)methyl-1-cyclohexanone from the Michael reaction of dimethyl malonate and cyclohexenone catalysed by Ru[(<i>R,R</i>)-Msdpen](hmb)	221
	Conclusion	222
	References	223
12	Stereoselective Hydroformylation, Carbonylation and Carboxylation Reactions	225
12.1	Ortho-diphenylphosphanylbenzoyl-(<i>o</i> -DPPB) directed diastereoselective hydroformylation of allylic alcohols <i>Bernhard Breit</i>	226
12.1.1	Synthesis of 1 <i>RS</i> -(±)-[(1-iso-propyl-2-methyl)prop-2-enyl] (2-diphenylphosphanyl)benzoate	227
12.1.2	Synthesis of (1 <i>R</i> *,2 <i>R</i> *)-(±)-[(1-Isopropyl-4-oxo-2-methyl)butyl] (2-diphenylphosphanyl)-benzoate	228
	Conclusion	229
	References	230
12.2	The synthesis and application of ESPHOS: A new diphosphorus ligand for the hydroformylation of vinyl acetate <i>Martin Wills and Simon W. Breeden</i>	230
12.2.1	Synthesis of <i>ortho</i> -diazobromobenzene	232
12.2.2	Synthesis of <i>ortho</i> -(dichlorophosphine) bromobenzene	232
12.2.3	Synthesis of <i>ortho</i> -bis(dimethylamino) bromobenzene	233
12.2.4	Synthesis of 1,2-bis(dimethylaminophosphanyl) benzene	234
12.2.5	Synthesis of ESPHOS (1) ^[2]	235
12.2.6	Hydroformylation of vinyl acetate ^[3]	236
	Conclusion	237
	References	237
12.3	Platinum-catalysed asymmetric hydroformylation of styrene <i>Submitted by Stefánia Cserépi-Szücs and József Bakos</i>	238

12.3.1	Rhodium-catalysed asymmetric hydroformylation of styrene	239
12.3.2	Synthesis of (4 <i>R</i> ,6 <i>R</i>)-4,6-dimethyl-2-chloro- 1,3,2-dioxaphosphorinane	240
12.3.3	Synthesis of (2 <i>R</i> ,4 <i>R</i>)-2,4-bis[(4 <i>R</i> ,6 <i>R</i>)-4,6-dimethyl- 1,3,2-dioxaphosphorinane-2-yloxy]-pentane	241
12.3.4	Determinataion of optical purity: synthesis of mixture of 2-phenylpropionic acid and 3-phenylpropionic acid	243
12.4	Phosphine-free dimeric palladium (II) complex for the carbonylation of aryl iodides <i>C. Ramesh, Y. Kubota and Y. Sugi</i>	244
12.4.1	Synthesis of the dimeric oximepalladacycle	244
12.4.2	Synthesis of phenyl biphenyl-4-carboxylate	245
	Conclusion	247
	Reference	247
12.5	Carboxylation of pyrrole to pyrrole-2-carboxylate by cells of <i>Bacillus megaterium</i> in supercritical carbon dioxide <i>Tomoko Matsuda, Tadao Harada, Toru Nagasawa and Kaoru Nakamura</i>	247
12.5.1	Construction of supercritical carbon dioxide reaction system	248
12.5.2	Carboxylation of pyrrole to pyrrole-2-carboxylate	249
	Conclusion	250
	References	250
	Index	251