

## Contents

<b>1</b>	<b>Oxidative Coupling – Bonding between Two Nucleophiles</b>	<b>1</b>
1.1	Introduction/General	1
1.1.1	What is Oxidative Cross-Coupling?	1
1.1.2	Why Oxidative Cross-Coupling?	1
1.1.3	How Does Oxidative Cross-Coupling Work?	3
1.1.4	Development and Outlook	4
	References	4
<b>2</b>	<b>Organometals as Nucleophiles</b>	<b>7</b>
2.1	Classification and Applications of Organometallic Reagents	7
2.2	Csp–M and Csp <sup>2</sup> –M as Nucleophiles	8
2.2.1	Alkyne–Alkyne Oxidative Coupling	9
2.2.1.1	Alkynyl-Si	11
2.2.1.2	Alkynyl-Sn	12
2.2.1.3	Alkynyl-B	14
2.2.1.4	Alkynyl-Mg	17
2.2.1.5	Alkynyl-Te	19
2.2.2	Alkyne–Cyano Oxidative Coupling	22
2.3	Csp <sup>2</sup> –M and Csp <sup>3</sup> –M as Nucleophiles	22
2.4	Csp <sup>2</sup> –M and Csp <sup>3</sup> –M as Nucleophiles	28
2.5	Csp <sup>2</sup> –M and Csp <sup>2</sup> –M as Nucleophiles	30
2.5.1	Homocoupling of Csp <sup>2</sup> –M	30
2.5.2	Cross-Coupling between Different Species of Csp <sup>2</sup> –M	32
2.6	Csp <sup>2</sup> –M and Csp <sup>3</sup> –M as Nucleophiles	34
2.7	Csp <sup>3</sup> –M and Csp <sup>3</sup> –M as Nucleophiles	37
2.8	Conclusions	40
	Acknowledgments	41
	References	42

<b>3</b>	<b>Oxidative Couplings Involving the Cleavage of C–H Bonds</b>	<b>45</b>
3.1	Theoretical Understandings and Methods in C–H Bond Functionalization	45
3.1.1	Introduction	45
3.1.2	Mechanisms of C–H Cleavage by Transition Metals	47
3.1.2.1	Oxidative Addition	49
3.1.2.2	Electrophilic Substitution	49
3.1.2.3	$\sigma$ -Bond Metathesis	52
3.1.2.4	Concerted Metalation Deprotonation (CMD)	52
3.1.2.5	1,2-Addition	55
3.1.2.6	Biomimetic C–H Oxidation	55
3.1.2.7	Carbenoid/Nitrenoid C–H Insertion	56
3.1.3	Methods for Selective C–H Bond Functionalization	58
3.1.3.1	Directed C–H Functionalization	58
3.1.3.2	Sterically Controlled C–H Functionalization	63
3.1.3.3	C–H Functionalization via Ionic Intermediates	63
3.1.3.4	C–H Functionalization via Radical Intermediates	67
3.2	Oxidative Couplings between Organometals and Hydrocarbons	71
3.2.1	C(sp)–H and Organometals as Nucleophiles	71
3.2.2	Csp <sup>2</sup> –H and Organometals as Nucleophiles	73
3.2.3	Csp <sup>3</sup> –H and Organometals as Nucleophiles	93
3.3	Oxidative Couplings between Two Hydrocarbons	95
3.3.1	C(sp)–H and C(sp)–H as Nucleophiles	95
3.3.2	C(sp)–H and C(sp <sup>2</sup> )–H as Nucleophiles	99
3.3.3	C(sp)–H and C(sp <sup>3</sup> )–H as Nucleophiles	105
3.3.4	Csp <sup>2</sup> –H and Csp <sup>2</sup> –H as Nucleophiles	106
3.3.4.1	Oxidative Coupling between Directing-Group-Containing Arenes and Unactivated Arenes	107
3.3.4.2	Oxidative Coupling of Arenes without Directing Groups	109
3.3.4.3	Intramolecular Oxidative Coupling of Unactivated Arenes	110
3.3.4.4	Oxidative Heck-Type Cross-Coupling	114
3.3.5	Csp <sup>2</sup> –H and Csp <sup>3</sup> –H as Nucleophiles	123
3.3.5.1	Intramolecular Oxidative Coupling between Aromatic Csp <sup>2</sup> –H and Csp <sup>3</sup> –H	123
3.3.5.2	Intramolecular Oxidative Coupling between Alkene Csp <sup>2</sup> –H and Csp <sup>3</sup> –H	125
3.3.5.3	Intermolecular Oxidative Coupling between Csp <sup>2</sup> –H and Csp <sup>3</sup> –H	127
3.3.6	C(sp <sup>3</sup> )–H and C(sp <sup>3</sup> )–H as Nucleophiles	128
3.4	Conclusions	130
	References	130
<b>4</b>	<b>Bonding Including Heteroatoms via Oxidative Coupling</b>	<b>139</b>
4.1	Introduction	139
4.2	Oxidative C–O Bond Formation	140

4.2.1	C–H and O–M as Nucleophiles	140
4.2.2	C–H and O–H as Nucleophiles	140
4.2.2.1	C(sp <sup>2</sup> , Aryl)–O Bond Formation	140
4.2.2.2	C(sp <sup>2</sup> , Heteroaryl, Alkenyl)–O Bond Formation	144
4.2.2.3	C(sp <sup>3</sup> , Benzyl)–O Bond Formation	145
4.2.2.4	C(sp <sup>3</sup> , Alkanes with Directing Group)–O Bond Formation	145
4.2.2.5	C(sp <sup>3</sup> , Ethers, Amines, Amides, Alkanes)–O Bond Formation	148
4.2.2.6	C(sp <sup>3</sup> , allyl)–O Bond Formation	148
4.3	Oxidative C–N Bond Formation	152
4.3.1	C(sp)–N Bond Formation	152
4.3.2	C(sp <sup>2</sup> , Arenes with Directing Group)–N Bond Formation	153
4.3.3	C(sp <sup>2</sup> , Simple Arenes)–N Bond Formation	156
4.3.4	C(sp <sup>2</sup> , Heteroaryl)–N Bond Formation	156
4.3.5	C(sp <sup>2</sup> , Alkenyl)–N Bond Formation	159
4.3.6	C(sp <sup>3</sup> , Alkyl)–N Bond Formation	163
4.3.7	C(sp <sup>3</sup> , Allyl)–N Bond Formation	164
4.4	Oxidative C–Halo Bond Formation	166
4.4.1	C–H and Halo–H as Nucleophiles	167
4.4.2	C–H and Halo–M as Nucleophiles	168
4.5	Oxidative C–S Bond Formation	170
4.5.1	C(sp <sup>2</sup> )–S Bond Formation	170
4.5.2	C(sp)–S Bond Formation	171
4.6	Oxidative C–P Bond Formation	172
4.6.1	C(sp <sup>2</sup> , Aryl)–P Bond Formation	172
4.6.2	C(sp <sup>2</sup> , Heteroaryl)–P Bond Formation	173
4.6.3	C(sp <sup>2</sup> , Alkenyl)–P Bond Formation	176
4.6.4	C(sp)–P Bond Formation	176
4.6.5	C(sp <sup>3</sup> )–P Bond Formation	176
4.7	Oxidative C–B Bond Formation	177
	References	178
<b>5</b>	<b>Oxidative Radical Couplings</b>	<b>185</b>
5.1	Introduction	185
5.2	Oxidative Radical C–C Couplings	185
5.2.1	Coupling of Csp <sup>3</sup> –H with Csp–H Bonds	185
5.2.2	Coupling of Csp <sup>3</sup> –H with Csp <sup>2</sup> –H Bonds	187
5.2.3	Coupling of Csp <sup>3</sup> –H with Csp <sup>3</sup> –H Bonds	200
5.2.4	Coupling of Csp <sup>2</sup> –H with Csp <sup>2</sup> –H Bonds	204
5.3	Oxidative Radical C–C Couplings through Cascade Process	208
5.4	Oxidative Radical C–C Couplings via C–C(N) Bond Cleavage	217
	References	222

