

Index

a

- acid anhydrides 212
- acid catalyzed synthesis, of thiazolo
 - [4,5-b]indol-2-amines 263
- acyl chlorides 212, 215, 217, 218
- acyl halides 212, 213
- 6-alkoxy piperidin-3-one 34–36
- aluminum trihalide 222
- β -amino- α,β -unsaturated ketone 176
- 2-aminobenzoates 421, 423
- 3-aminobenzothiophenes 422, 476, 477
- 3-aminoindazoles
 - cascade denitrogenative transannulation/hydrolyzation 420, 421
- Cu-catalyzed aromatic metamorphosis 475
- Cu-catalyzed denitrogenative transannulation 476, 477
- denitrogenation of
 - cyanoarylated oxindoles synthesis 418
 - isoquinolinones synthesis 418, 419
- denitrogenative ring-opening of
 - aromatic nitrile-containing (hetero)arenes synthesis 415
- C3-cyanoarylation of
 - quinoxalin-2(1*H*)-ones 416
- C–H cyanoarylation of enamines 417
 - for nitrile-containing triphenylenes and fluorenes synthesis 416
 - olefinic C–H cyanoarylation of ketene dithioacetals 417
- denitrogenative transannulation of 418–422
- denitrogenative transformations
 - cascade radical process 418, 419
 - coupling with enamines 417
 - coupling with heterocycles and arenes 415–416
 - coupling with ketene dithioacetals 417
 - coupling with thiols and diselenides 419
 - synthetic value and challenges 414
- N–N bond cleavage of 421–423
- oxidative denitrogenative radical coupling 419
- oxidative N–N bond cleavage of 422, 423
- synthesis 17–18
- 1-aminoisoquinolines 422, 476, 477
- 2-aminophenol 7
- 3-aminoquinolines 38, 153
- (2-aminovinyl)imidazoles 99
- [4+2]-annulation of benzamides and 3-diazoindolin-2-imines 261, 262
- [4+1]-annulation of diazoimines with 2-(arylamino)ethanols 270

- arenes
 - intermolecular annulation of
 - with 4-phthalimido-1-sulfonyl-1,2,3-triazoles 86
 - with 1-sulfonyl-1,2,3-triazoles 86
 - with Rh-AVCs, dearomatizing intramolecular annulation of 85
 - arene-triazole-triazole hybrids 85
 - aromatic metamorphosis 416
 - aromatic nitrile-containing (hetero) arenes 415
 - 2-(3-arylallylidene)-3-oxindoles 253, 254
 - arylepoxides 101, 109
 - (*E*)-3-arylideneindolin-2-imines 276
 - 3-arylideneoxindoles 149
 - β -arylpyrrolidines 118, 234, 235
 - aryltiiranes 109
 - aspidosperma and kopsia indole alkaloids 493–495
 - asymmetric C–H insertion
 - of silicon-substituted alkanes 235
 - of unactivated sp^3C –H bonds 233
 - asymmetric functionalization, of metallocarbenes 228
 - asymmetric synthesis
 - of chiral carbon isotope hydrocarbons 232
 - of (+)-Lysergol 245
 - of oxazolines 237
 - of pyrroloindolines via formal [3 + 2]-cycloaddition 237
 - atom transfer reactions 242, 243
 - ($\pm$)-aurantioclavine 495
 - aza-Diels–Alder reaction 193
 - azadiene formation
 - 4-aminooxazolidinones synthesis 196, 197
 - butenolide tethered homotryptamine derivatives synthesis 197, 199
 - 1,2-dihydropyridine derivatives 193, 195
 - N*-heterocycles 196, 198
 - Rh-AVCs
 - 1,2-acyl migration in 195, 196
 - 1,2-aryl migration 199, 200
 - ring expansion and rearrangement reactions in 193, 194
 - 1,2-sulfur migration in 193, 195
 - 8-azaheptafulvenes, transannulation of 90
 - azahexatrienes 92
 - aza-[2,3]-sigmatropic rearrangement 182, 205
 - azepino-fused diindoles 39
 - azide-alkyne cycloaddition reactions 227
 - 2*H*-azirines 105, 106
- b**
- Banert Cascade 3
 - benzodiazepine-indolinetriazonane 178, 180
 - 1,2-benzodithiol-3-ones synthesis 399–400
 - benzopyrrolizidine ring system 180
 - 1,2,3-benzotriazin-4(3*H*)-ones
 - biaryl sultams synthesis 404–406
 - 3,4-dihydro-1,2-benzothiazine-1,1(2*H*)-dioxides 403–404
 - electrochemical denitrogenative transformations 402
 - of 3-iminothiaisindoline-1,1-dioxides 403
 - Lewis acid mediated denitrogenation reactions 401–402
 - metal-catalyzed denitrogenative transformations 381–382
 - metal-free denitrogenative transformations 398–400
 - nickel and palladium-catalyzed denitrogenative transannulation reactions 382–388
 - nickel-catalyzed denitrogenative cross-coupling reactions 388–394
 - Pd-catalyzed cross-coupling reactions 394, 395
 - thermolysis reaction 400, 401
 - visible-light mediated denitrogenative reactions 395–398
 - benzotriazinones, synthesis of 18–20

benzotriazole ring cleavage (BtRC) 216, 327, 344

benzotriazoles

- AlCl₃-mediated cyclization 344, 345
- BtRC-mediated synthesis 346, 348
- Cu-catalyzed denitrogenative cyclization reaction 336, 339
- fundamental properties of 326
- FVP 344, 346, 347
- HMPA 347, 349
- industrial applications 325
- Ir-catalyzed cycloaddition 330, 332
- NBS-promoted synthesis 347, 349
- Pd-catalyzed carbonylative cyclization 336, 338
- Pd-catalyzed cycloaddition 330, 331
- Pd-catalyzed [2+2+1]-cycloaddition 333
- Pd-catalyzed [2+2+2]-cycloaddition 333, 334
- Pd-catalyzed [3+2]-cycloaddition 335–337
- precursors 328–330
- quinoxalines synthesis 340, 341
- ring cleavage strategy 325, 327
- synthesis 12, 13
- using industrial waste PMHS 343
- using (TMS)₃SiH 341, 343
- using stannane 340, 342

BF₃·Et₂O catalyzed arylation, of

- 3-diazoindolin-2-imines with arylaldehydes 272, 273

biaryl sultams synthesis 404–406, 450, 452, 453

bicyclic aziridines 106, 107

1,3'-biindoles synthesis 264, 265

bimetallic relay catalysis mechanism 240, 241

boron trifluoride 221

2-bromo-1-sulfonyl imidazole 43

Bronsted acid catalyzed reactions 312–315

Buchwald–Hartwig-type chemistry 328

C

carbenes, structure and types of 189, 190

catalytic reaction mechanism, of

- pyrazoles with 1-sulfonyl-1,2,3-triazoles 99, 100

(-)-chanoclavine I 489–490

C–H cyanoarylation, of enamines 417

CH-insertion of Rh-AVCs

- acridones *via* intramolecular 126
- allylic C–H bonds 117, 118
- 2-aminobenzofuran derivatives 124
- 3-aminocarbazoles *via* 6 π -electrocyclization 131

anilines 124

arenes 123

aromatic C–H bonds of anilines 121

aryl ethers 122

atroposelective Rh(III)-catalyzed 129

azulenes 122

benzofulvenes *via* intramolecular 126

benzylic C–H bonds 118

catalyst-free thermal CH-insertion 127

C2–H bond of indole 133

C3–H bond of indole 133

β -C–H bonds in silanes 119

α -C–H bonds of ethers 120

chemoselective intramolecular 123

diazepane annulation *via* intramolecular 132

1,2-dihydro- β -carboline based on organocatalytic cyclization 131

dihydroindoles *via* intramolecular insertion 125

distal allylic/benzylic C–H bonds 119

electron-rich azaheterocycles 130

fluorenes *via* intramolecular 126

indanones and tetralones *via* intramolecular 124

indole C–H bonds 127

indole preparation *via* intramolecular insertion 125

intramolecular *aza*-Michael addition 130

intramolecular transannular 117

CH-insertion of Rh-AVCs (*contd.*)

- of *N*-benzylanilines 120
- one-pot conversion 132
- Rh(III) catalysis 129
- saturated 5-membered (hetero)cycles
 - via* intramolecular 120, 121
- tryptamine derivatives 128
- chiral sulfinylamidines 242, 243
- cobalt-catalyzed transannulation of
 - pyridotriazoles 302–303
- copper-catalyzed [4 + 1]-annulation of
 - enaminothiones with diazoimines 268, 269
- copper catalyzed denitrogenative
 - transannulation of pyridotriazoles
 - with alkynes 299–300
 - with amines and amino acids 300–302
- copper-catalyzed synthesis
 - of aromatic nitrile-containing (hetero)arenes 473–475
 - of 3,3-diaryl-2-imino-indoles 255, 256
 - of disubstituted indanones 476–478
 - of 3,3-disubstituted indoline derivatives 257, 259
 - of 3-indolyl-4*H*-chromen-4-ones 265
 - of spiro[cyclopropane-1,3'-indolin]-2'-imines 268, 269
- copper/TBHP oxidation system 424
- crypto-optically active compounds 232
- C/X–H insertion reactions of azavinyl
 - carbenes 116
- C–X or X–X bonds azavinyl carbenes
 - insertion reactions
 - 1,3-difunctionalization 172–180
 - [2,3]-sigmatropic rearrangement reactions 180–183
 - thioacetals *via* S–S bond insertion reaction 184
- cycanoarylated oxindoles 418
- cyclic ammonium ylide 180
- cyclic enaminones 217, 218
- (*R*)-cycloprodigiosin 244, 485–486
- cyclopropanation/cope rearrangement 68, 88, 89
- cyclopropylmethanamines 230, 231

d

- denitrogenative process 327, 328, 335, 336, 340, 349
- diaryl ether-triazole hybrids 86
- diastereoselective synthesis 58
 - of oxabicyclo[2.2.1]heptene core 36
 - of spiroindanones 41
- 2-(1-diazoalkyl)benzoxazoles 157, 158
- diazo compounds 13, 55, 79, 116, 171, 180, 191, 192, 227, 228, 236, 251, 255, 257, 268, 272, 273, 275, 281, 283, 313, 316–318
- α -diazoimines 31, 116, 191
- diazoimines with allyltrimethylsilanes 273, 274
- 3-diazoindolin-2-imines
 - annulation reactions 260–271
 - C–H bonds insertion reactions 255–258
 - C–X bonds insertion reactions 257–260
 - indole embedded α -imino metal carbenoid 251, 252
 - synthesis of 251–252
 - X–H bonds insertion reactions 253–255
- dichlorobenzene (DCB) 310
- dichloroethane (DCE) 310
- 3,3-difluoroallyl sulfide 182, 183
- 1,3-difunctionalization 172–180
- 3,4-dihydro-1,2-benzothiazine-1,1(2*H*)-dioxides 403–404, 407
- dihydrofuran ring 91
- dihydromorpholines 173, 174
- 1,2-dihydropyridines 92, 193
- 2,3-dihydropyrroles 53, 56, 58, 66, 67, 211, 212, 229, 238, 239
- dihydropyrroles, synthesis 33, 34, 53
- dihydrothiazines 173, 174
- 2,3-diiminoindoles from diazoimines
 - and benzo[*c*]isoxazoles 275, 276
- 1,3-diketones 39, 144, 146
- Dimroth rearrangement 6, 171, 172, 192, 227

Dimroth-type equilibrium 31, 325, 327, 330, 335, 349
 diphenyl phosphorazidate (DPPA) 5
 distal site-selective $\delta\text{C-H}$ insertion of allylic alcohols 236
 2,5-disubstituted furan and dihydrofuran 261
 2,2-disubstituted indanones 419–421, 476
 2,6-di-*tert*-butyl-4-methyl pyridine (DTBP) 229

e

electrochemical denitrogenative transformations 402–403, 406
 electron-withdrawing and electron-donating groups (EWG & EDG) 344
 β -enamido halides 212
 β -enamido triflates 212–214
 enantioselective synthesis
 of α -aminoketones 240, 241
 of β/γ of amino acid derivatives 240
 of cycloprodigiosin 244
 of (*R*)-cycloprodigiosin 485–486
 of cyclopropylmethanamines 230, 231
 of dihydro- β -carboline 242
 of 2,3-dihydropyrroles 238, 239
 of piperidine-fused *trans*-cycloalkanes 230
 2,5-epoxy-1,4-benzoxazepines 37

f

Fe-catalyzed intermolecular denitrogenative annulation 434
 Fischer-type carbenes 189, 190
 flash vacuum pyrolysis (FVP) 344, 346, 347, 350, 427, 447
 flash vacuum thermolysis (FVT) 318, 319
 β -fluoroacylenamido triflates 212, 214
N-fluoroalkylated imidazoles 219
N-fluoroalkylated indoles 220
 2-fluoroalkyl-imidazoles 216
N-fluoroalkyl ketenimines 219, 223

N-fluoroalkyl-1,2,3-triazoles, denitrogenation of 218–223
 furans
 with cyclohexenyl-substituted Rh-AVCs 89
 to pyrroles 91
 ring opening routes 90
 with 1-sulfonyl-1,2,3-triazoles 91
 3,4-fused indole skeletons 487–489

g

glycidols 102, 143, 144, 173
 gold catalyzed synthesis of
 2-iminoindolin-3-ones 273, 275
 ($\pm$)-GSK1360707 493

h

heteroaromatic rings 90–101
 hexafluoroisopropanol (HFIP) 236
 hexamethylphosphoramide (HMPA) 347
 hydrolysis reaction or *aza*-Friedel-Crafts reaction 181
 2-hydroxy-*N*-substituted benzamides synthesis 399, 400

i

imidazoles synthesis 42, 44, 97, 98
 imidazolidines 107
 imidoyl halides 221, 222
 imines, (2 + 2 + 2) annulations of 375–376
 α -imino carbenoids 192
 3-iminocyclopropenes 285, 286
 3-iminothiaisoindoline-1,1-dioxides 403, 407
 indole alkaloids, aspidosperma and kopsia 493–495
 indole embedded α -imino metal carbenoid 251, 252
 indoles
 C-H bond of 88
 with Rh-AVCs 88
 with 1-sulfonyl-1,2,3-triazoles 87
 indolo[2,3-*c*]isoquinolin-5-ones 261

- intermolecular denitrogenative
 - annulation of pyridotetrazoles 433–435
 - via Mn-nitrene intermediate 432–433
- intermolecular transannulation, of
 - N*-sulfonyl-1,2,3-triazoles
 - with alkenes
 - asymmetric cyclopropanation of aryloxy triazoles with styrenes 54
 - asymmetric cyclopropanation of triazoles with pinacol allyl boronates 54
 - asymmetric cyclopropanation of triazole with styrenes 53
 - asymmetric cyclopropanation reactions of triazoles 52
 - catalyst-free diastereoselective cyclopropanation of 4-phthalimido-*N*-sulfonyl triazoles 55
 - enantioselective synthesis of C3-symmetric triangular macrocycles 55
 - mechanism for Rh (II) catalyzed synthesis of THF-DPs and THP-DPs 58, 59
 - mechanism of Rh (II) catalyzed transannulation for pyrrole synthesis 60
 - Rh(II)-catalyzed dihydropyrrole synthesis from electron-rich styrene and triazoles 57
 - Rh (II)-catalyzed piperidine-fused *trans*-cycloalkenes synthesis from triazoles and MCPs 61
 - Rh(II) catalyzed reaction of triazole tethered with MCP 63
 - Rh(II) catalyzed synthesis of piperidine-fused *trans*-cycloalkene 61
 - Rh (II)-catalyzed tandem cycloisomerization of methylenecyclopropyl triazoles 62
 - Rh(II)-catalyzed transannulation of triazoles tethered with MCP 62
 - Rh (II)-catalyzed transannulation of triazoles with acyclic vinyl ethers 59
 - Rh (II)-catalyzed transannulation of triazoles with cyclic vinyl ethers 58
 - Rh (II) catalyzed transannulation of triazoles with *N*-vinyl indoles 56, 57
 - Rhodium (II)-catalyzed dihydropyrrole synthesis from methoxystyrene 56
 - synthesis of dihydropyrroles from *NH* triazoles 53
 - with alkynes
 - Ni-catalyzed transannulation of 70
 - Rh(II)/Ag(I)-catalyzed transannulation of triazoles 71
 - Rh (III)-catalyzed dual C(sp²)-H bond activation of 4-aryl-*N*-sulfonyl-1,2,3-triazoles 72
 - Rh (III)-catalyzed dual C(sp²)-H bond activation of triazoles 72, 73
 - with allenes 75
 - isopyrroles treatment with electrophilic agents 76
 - mechanism of Ni-catalyzed transannulation of triazoles 77
 - nickel catalyzed transannulation of triazoles 76
 - Rh(II)-catalyzed transannulation of triazoles 77
 - with 1,3-dienes
 - Rh(II)-catalyzed reactions of triazoles with cyclic silyl dienol ethers 67
 - Rh(II)-catalyzed transannulation of 4-alkenyl-triazoles 65
 - Rh(II)-catalyzed transannulation of 4-aryl-*N*-sulfonyl-triazoles 66
 - Rh(II)-catalyzed transannulation of triazoles 67

intramolecular denitrogenative C(sp³)-H
amination of pyridotetrazoles
435–437

intramolecular transannulation
with alkenes 63–64
with alkynes
Rh(II) catalyzed intramolecular
transannulation of triazoles 73,
74
silver catalyzed intramolecular
cyclization of 4-(2-ethynylaryl)-
N-sulfonyl-1,2,3-triazoles 74,
75
with allenes 78, 79
with 1,3-dienes 68–69
o-iodoacetanilide 216, 217
5-iodo-1,2,3-triazoles
insertion reactions 156–159
insertion reactions of 156–159
synthesis 10–11
2-(5-iodotriazolyl)benzoic acids 159
Ir-catalyzed denitrogenative C(sp²)-H
amination of pyridotetrazoles
429–431

iron-catalyzed intermolecular
benzylic C(sp³)-H amination
441–442

iron catalyzed intermolecular
denitrogenative C–N cross
coupling reactions 443–444

iron-catalyzed intramolecular
denitrogenative radical C(sp²)-H
amination of pyridotetrazoles
439–440

iron-catalyzed intramolecular
denitrogenative radical
rearrangement, of pyridotetrazoles
437–438

isoquinoline fused indoles synthesis
261

isoquinolinones 418, 419

isoxazoles, transannulation of
to pyrroles 93
with Rh-AVCs 94, 95
with 1-sulfonyl-1,2,3-triazoles 96

k

ketenimine formation 206–208

l

Lewis-acid catalyzed reactions

BF₃·OEt₂ 309, 310

indium triflate In(OTf)₃ 311

isothiocyanates 312

Lewis acid mediated denitrogenation
reactions 401–402

Lewis or Brønsted acids 211

(+)-lysergol 244, 245, 488

m

1-mesyl-4-substituted-1,2,3-triazole 230

metal carbenoids

bonding and types of 190

from diazo compounds 191, 192

electronic properties 189

Fischer-type carbenes 189

α-imino metal carbenoids 191–193

N-heterocyclic carbenes 190

radical carbenes 190

Schrock-type carbenes 190

metal catalyzed α-imino metal carbene
intermediate 51, 52

metal-catalyzed transannulation of
pyridotriazoles 282

metal-free denitrogenative
transformations

1,2-benzodithiol-3-ones synthesis
399–400

2-hydroxy-N-substituted benzamides
synthesis 399, 400

N-isoxazolyl-2-iodobenzamides and
4*H*-Tetrazolo[1,5-*a*] [1,4]
benzodiazepine-6-ones 398

methylenecyclopropane 61, 230

β-(methylthio)-α,β-unsaturated ketone
176

Mn-catalyzed denitrogenative annulation,
of pyridotetrazoles 432

Morita–Baylis–Hillman adduct 240

multisubstituted N-sulfonyl-1,2,3-
triazoles 8

n

- N1-acetylbenzotriazole 217
- N*-acylamidines 46
- nakafuran-8 245, 246, 496–497
- N*-cyanosulfoximines 43, 44
- newbouldine 498–499
- N*-heterocyclic carbenes (NHCs) 190
- NH-insertion of Rh-AVCs
 - 3-aminopyrroles 151
 - anilines 150
 - carbazoles 150
 - 2,3-dehydropiperazines 152
 - β -enamino esters 151
 - β -enaminones 152
 - formal 1,3-insertion 149
 - 2-(hydroxymethyl)anilines 152, 153
 - to 2-vinylanilines 152, 153
- NH*-1,2,3-triazoles
 - with acyl halides 213
 - denitrogenation of 211–218
 - with fluorinated acid anhydrides 214
 - 3-fluoroalkyl-1,2,4-triazines 215, 216
 - with thiophosgene 217
 - and trichloroacetic anhydride 215
 - with trifluoroacetic anhydride 216
 - with triphosgene 218
- NH*-triazoles, synthesis 1–6
- nickel and palladium-catalyzed
 - denitrogenative transannulation reactions
 - isindolin-1-ones and related derivatives 386–388
 - isoquinolones and related derivatives 382–385
 - phenanthridinones synthesis 385–386
- nickel-catalyzed denitrogenative cross-coupling reactions
 - functionalized β -aryl ketones 392–394
 - ortho*-arylated, alkylated and alkenylated benzamides 388–392
- N*-isoxazolyl-2-iodobenzamides synthesis 398
- nonaromatic rings 89–90
 - O,N,S-nonaromatic rings 101–110
- N*-sulfonyl-triazoles 191
- N*-sulfonyl-1,2,3-triazoles
 - and aldehydes 32
- alkenes
 - intermolecular transannulation with 52–63
 - intramolecular transannulation with 63–64
- alkynes
 - intermolecular transannulation with 69–73
 - intramolecular transannulation with 73–75
- allenes
 - intermolecular transannulation with 75–78
 - intramolecular transannulation with 78, 79
- atom transfer reactions 242–243
- as carbene precursor 31, 32
- with carbonyls 31–42
- carbonyls and nitriles 44–47
- denitrogenative rearrangements of
 - through azadiene formation 193–200
 - through ketenimine formation 206–207
 - through ylide formation 201–206
 - through zwitterionic intermediate 200–201
- 1,3-dienes
 - intermolecular transannulation with 65–67
 - intramolecular transannulation with 68–69
- with 1,3-diketones 39
- with isocyanates and isothiocyanates 44, 45
- natural product and total synthesis 243, 246
- with nitriles 42–44
- relay catalysis 240–242
- rhodium-catalyzed C–H insertion reactions 233–236
- rhodium-catalyzed cyclopropanation reactions 227–232

rhodium-catalyzed transannulation reactions 236–239
 synthesis of 6–9
 and thionoesters 46
 N1-sulfonyl-1,2,3-triazoles insertion reactions
 B–H insertion 154–155
 C–H insertion 116–133
 N–H insertion 149–154
 O–H insertion 133–149
 Si–H and P–H Insertion 155–156
N-tosyl hydrazones 4, 191
N-trifluoromethyl-1,2,3-triazoles, synthesis of 8–10

O

octahydro-purine derivative 175
 O–H insertion reactions of Rh-AVCs
 2-acyl-2,5-dihydropyrroles 140, 141
 benzoquinone derived allyl alcohols 139
 benzyl alcohols 141, 142
 Claisen rearrangement 137
 Domino reactions 142, 143
 formal 1,3-insertion 135
 2-furfuryl alcohols 141
 γ -hydroxyacrylates and MBH adducts 138
 glycidols 143, 144
 halohydrins 144, 145
 Mukaiyama aldol reaction 136
 propargyl alcohols 140, 141
 4-vinyl benzoxazinanones 147
 olefinic C–H cyanoarylation, of ketene dithioacetals 417
 one-pot enantioselective synthesis, of 2,3-dihydropyrroles 238
 O,N,S-nonaromatic rings 101–110
 organoselenium compounds 182
ortho-methylated benzamides synthesis 394, 395
ortho-phosphorylated aryl amides synthesis 396, 397
ortho-selenylated benzamides synthesis 397–398

oxabicyclo[2.2.1]heptene core 36
 oxazolines 32, 236, 237
 oxetanes 102, 103, 173–175
 oxidative denitrogenation/intramolecular radical cascade 416
 2-oxopyridines with triazoles 179, 180
 β -oxyenamine 148
 α -oxygenated amidines 456–459

P

palladium-catalyzed denitrogenative process 335
 palladium-catalyzed ring opening of pyridotriazole
 with acetic anhydride 297–298
 with aryl halides 294–297
 of [1,2,3]triazolo[1,5-*a*]pyridines 293–294
 palladium-catalyzed synthesis of 3-haloindol-2-amines 260
 Pd(II)-catalyzed arylation of diazoimines with arylboronic acids 271, 272
 Pd-catalyzed cross-coupling reactions
 ortho-arylated and alkenylated benzamides 394
 ortho-methylated benzamides synthesis 394, 395
N-perfluoroalkyl-1,2,3-triazoles 9, 10
 (+)-petromyroxol 181, 182, 491–493
 phenanthridine derivatives 336, 350
 phenanthridines 463, 466
 phenanthridinones synthesis 385–386, 400
 4-phenyl-*N*-sulfonyl-1,2,3-triazoles 233
 photo-induced denitrogenative transformations
 indole alkaloid framework 497–498
 photolysis 191, 255
 and thermolysis, of pyridotriazoles 316–319
 pinacol allyl boronate 54, 230
 piperidine-fused *trans*-cycloalkanes 61, 230
 polymethylhydrosiloxane (PMHS) 343, 344, 350

poly-nitrogen heterocycles
 denitrogenative transformations 413
 radical denitrogenation
 of benzotriazinones and
 benzothiatiazines 449–456
 of pyridotriazoles 467–472
 of substituted 3-aminoindazoles
 473–479
 of triazoles and benzotriazoles 454,
 456–467
 5*H*-pyrazino[2,3-*b*]indoles synthesis 264
 pyridotetrazoles 428
 denitrogenative annulation
 via metalloradical mechanism
 433–444
 via Mn-nitrene intermediate
 432–433
 Ir-catalyzed denitrogenative
 C(sp²)—H amination 429–431
 synthesis 15–16
 pyridotriazoles
 acid-catalyzed denitrogenative
 transformation
 Bronsted acid-catalyzed reactions
 312–315
 Lewis-acid catalyzed reactions
 309–312
 cobalt-catalyzed transannulation
 302–303
 copper catalyzed denitrogenative
 transannulation
 with alkynes 299–300
 with amines and amino acids
 300–302
 denitrogenative transformations
 coupling of boronic acids 315, 316
 iodine and bromine 315–317
 thermolysis and photolysis 316–319
 light-induced transformations
 319–321
 metal-catalyzed transannulation 282
 photolysis and thermolysis 316–319
 radical denitrogenation 467–472
 rhodium (Rh)-catalyzed
 transannulation

alkyl silane 283
 with alkynes 283, 284
 with amine and amides 287–288
 with 1,3-dienes 290–291, 293
 with nitriles 284, 285
 with *N*-phenylbenzimidamides
 291, 294
 with phenyl 2-pyridine and *S*-aryl
 sulfoximines 288–292
 with propargyl alcohols 292–293
 ring-chain isomerization 309, 310
 synthesis 11–12
 (fused)pyrroles, substrate-controlled
 synthesis of 40

q

quinazolines
 from benzo[*c*]isoxazoles 97
 synthesis 96

r

radical carbenes 189, 190
 radical denitrogenative transformations
 of poly-nitrogen heterocycles
 benzotriazinones and
 benzothiatiazines 449–456
 pyridotriazoles 467–472
 substituted 3-aminoindazoles
 473–479
 triazoles and benzotriazoles 454,
 456–467
 relay catalysis 240–242
 Rh(II) catalysts 44, 69, 116, 172, 196,
 197, 211
 Rh(II)-catalyzed denitrogenative
 transannulation of
 benzo[*d*]isoxazoles 267
 Rh(II)-catalyzed Sommelet–Hauser
 type rearrangement reaction 182,
 183
 rhodium 2-azavinylcarbenes (Rh-AVCs)
 83–85
 azadiene formation
 1,2-acyl migration in 195, 196
 1,2-aryl migration 199, 200

- ring expansion and rearrangement
 - reactions in 193, 194
 - 1,2-sulfur migration in 193, 195
- CH-insertion (*see* CH-insertion of Rh-AVCs)
- generation and transannulation
 - reactions 84
- 1,3-hydroxy and acyloxy migration in 200
- isoxazoles, transannulation of 94, 95
- NH-insertion (*see* NH-insertion of Rh-AVCs)
- O–H insertion (*see* O–H insertion reactions of Rh-AVCs)
- rhodium carbenes 33, 38, 40–42, 220, 275, 291
- rhodium carbenoid intermediate
 - formation 282
- rhodium (Rh)-catalyzed [4+1]-annulation of 3-diazoindolin-2-imine with *o*-acylaniline 270
- rhodium (Rh)-catalyzed C–S bond insertion of 3-diazoindolin-2-imines with thioesters 259
- rhodium (Rh)-catalyzed denitrogenative annulation of monocyclic tetrazoles 428, 429
- rhodium (Rh)-catalyzed denitrogenative hydration of STs 134
- rhodium (Rh)-catalyzed reactions 92
 - C–H insertion reactions 233–236
 - cyclopropanation reactions 227–232
 - of diazoimines with aryl- and acrylaldehydes 271, 272
 - of 3-diazoindolin-2-imines
 - with aniline derivatives 258, 259
 - with 1,3-dienes 266
 - with 2*H*-azirines 264
 - of sulfoximines with
 - 3-diazoindolin-2-imines 263
 - of 1,2,3-thiadiazoles with
 - phosphaalkynes 376–377
 - transannulation reactions 236–239
- rhodium (Rh)-catalyzed reactions of 1,2,3-thiadiazoles
 - with alkenes
 - α,β -enals 367
 - Ir-catalyzed diastereospecific and enantioselective (3 + 2) transannulations 366, 367
 - regioselective synthesis of dihydrothiophenes and thiophenes 363–366
 - with alkynes for synthesis of
 - 4*H*-thiopyran-4-ones 362–363
 - multisubstituted furans and thiophenes 361–362
 - multisubstituted thiophenes 359–360
 - 5,*n*-fused thiophenes 361
 - with aziridines 377–378
 - with carbonyl compounds 368
 - with imines 375–376
 - with nitriles
 - 3-(alk-1-enyl)isothiazoles synthesis 374–375
 - bicyclic isothiazoles synthesis 372–373
 - with cyanoepoxides 373–374
 - for isothiazole synthesis 369–371
- rhodium (Rh)-catalyzed stereoselective diaminoenones synthesis 40, 41
- rhodium (Rh)-catalyzed synthesis, of
 - azepino, azocino and azonino-diindoles 267, 268
- rhodium (Rh)-catalyzed transannulation of pyridotriazoles
 - alkyl silane 283
 - with alkynes 283, 284
 - with amine and amides 287–288
 - with 1,3-dienes 290–291, 293
 - with nitriles 284, 285
 - with *N*-phenylbenzimidamides 291, 294
 - with phenyl 2-pyridine and *S*-aryl sulfoximines 288–292
 - with propargyl alcohols 292–293
- rhodium (Rh)-catalyzed transformation of diazoimines with nitrosoarenes 276
- of 3-diazoindolin-2-imines 260

- ring cleavage strategy 325, 327
- ring opening, transannulation with
 - heteroaromatic 90–101
 - O,N,S-Nonaromatic 101–110
- ring retention
 - aromatic and heteroaromatic 85–89
 - nonaromatic 89–90
- Ru(II)-catalyzed synthesis, of fused
 - α -carboline 270, 271
- ruthenium (Ru) catalyzed
 - transannulation, of pyridotriazoles with naphthoquinones 303–305
- S**
- Schrock-type carbenes 190
- selenonium ylide 182
- [2,3]-sigmatropic rearrangement reactions 180–183
- Si–H and P–H insertion 155–156
- single electron transfer (SET) 302, 333, 346, 395, 461, 463, 468, 469, 474
- spiro-2*H*-azirines 104, 106
- spiroindanones 41
- 6-substituted piperidin-3-ones 35, 36
- β -sulfanyl enamide 175–176
- 1-sulfonyl-1,2,3-triazoles, Rh(II)-catalyzed
 - reaction of
 - with spiro-2*H*-azirines 104, 106
 - with thiochromones 109, 110
 - with tiiranes 109, 110
 - with 1,3,5-triazinanes 109
- t**
- tetrabutylammonium fluoride (TBAF) 487
- [6,5,5,6]-tetracyclic spiroindolines 44, 45
- tetrahydrofurans 174, 492
- 1,2,4,5-tetrazines 413
- tetrazoles, synthesis of
 - 1*H*-tetrazoles 13–14
 - pyridotetrazoles 15, 16
 - tetrazolo[1,5- α]quinolines 16–17
 - 4*H*-tetrazolo[1,5- α] [1,4]
 - benzodiazepine-6-ones 398
 - tetrazolo[1,5- α]quinolines, synthesis of 16–17
- thermolysis 191
 - of 1,2,3-benzotriazin-4(3*H*)-ones 400, 401
 - and photolysis of pyridotriazoles 316–319
- 5*H*-1,2,3-thiadiazoles, Ag-mediated
 - annulation of 368
- 1,2,3-thiadiazoles, Rh-catalyzed
 - reaction of
 - with alkenes 363–368
 - with alkynes 359–363
 - with aziridines 377–378
 - with carbonyl compounds 368
 - with imines 375–376
 - with nitriles 369–375
 - with phosphalkynes 376–377
 - synthesis of 13
 - with unsaturated compounds 360
- 1,3-thiaphospholes, synthesis of 376–377
- thiavinyl carbenes 13, 362, 372, 378
 - Rh-catalyzed 359–360
- thiazolines, synthesis of 377–378
- 1,2-thiobenzonitriles 419, 420, 474
- thioketenes, (2 + 2 + 2) annulations of 375–376
- thionoester 46, 176
- total synthesis, of natural products
 - ($\pm$)-aurantioclavine 495
 - (-)-chanoclavine I 489–490
 - of (+)-lysergol 488
 - nakafuran-8 496, 497
 - newbouldine and withasomnine 498
 - (+)-petromyroxol 491–493
 - tuberostemopsioline and stemona-lactam R 490–491
- transannulations of *N*-sulfonyl-1,2,3-triazoles

- alkenes
 intermolecular transannulation with 52–63
 intramolecular transannulation with 63–64
- alkynes
 intermolecular transannulation with 69–73
 intramolecular transannulation with 73–75
- allenes
 intermolecular transannulation with 75–78
 intramolecular transannulation with 78, 79
- 1,3-dienes
 intermolecular transannulation with 65–67
 intramolecular transannulation with 68–69
- transition metal catalysis 1, 69, 191
- transition metal-catalyzed cross-coupling reactions 326
- 1,3,5-triazinane ring system 175
- 1,2,3-triazoles, synthesis of
 benzotriazoles 12, 13
 5-iodo-1,2,3-triazoles 10–11
 NH-triazoles 1–6
 N-sulfonyl-1,2,3-triazoles 6–9
 N-trifluoromethyl-1,2,3-triazoles 8–10
 pyridotriazoles 11–12
 triazoloindoles 12
- triazoloindoles synthesis 12
- 1,2,4-triazolyl-substituted-1,2,3-triazoles 229
- 3-((trifluoromethyl)thio)-2-aminoindoles 273, 274
- N*-triflyl azavinyl carbenes
 reactivity of 229
 rhodium(II) 238
- 2-trimethylsilyl-1,2,3-triazoles 215
- 1,3,5-trioxane 103, 175, 176, 184
- Tröger bases 108, 178, 180, 184
- tuberostemopsiroline and stemona-lactam
 R 490–491
- U**
- Uhle's ketone synthesis 487
- V**
- vibrational circular dichroism (VCD) 232
- 4-vinyl benzoxazinanones 147, 148
- visible-light-induced C(sp²)-P bond formation, by
 denitrogenative coupling reactions 463, 465
- visible-light-induced denitrogenative phosphorylation, of
 benzotriazinones 454
- visible-light mediated denitrogenative reactions
 isoquinolones synthesis 395–396
 ortho-phosphorylated aryl amides synthesis 396
 ortho-selenylated benzamides synthesis 397–398
- visible-light-mediated *ortho*-functionalizations 461, 462
- visible-light-promoted denitrogenative *ortho*-selenylation
 of benzotriazinones 453, 455
 of 1,2,3-benzotriazin-4(3*H*)-ones 397, 398
- W**
- withasomnine 498–499
- Y**
- ylide formation
 4-bromo-1,2-dihydroisoquinolines synthesis 201, 202
 dihydroisoquinoline and 2-aminoindanone derivatives 203

functionalized enamides synthesis

204, 205

Grob-type fragmentation of oxonium

ylides 205, 206

indole-substituted indanones synthesis

204

N-substituted 2-pyridones synthesis

205, 206

2-tetrasubstituted saturated

heterocycles synthesis 201, 202

Z

zwitterionic intermediate

azepane derivatives 200, 201

1,3-hydroxy and acyloxy migration in

Rh-AVCs 200



















