

## Index

### **a**

- AA +BB type polycondensation 259  
 AA-type monomer 259  
 4-acetylpyridine *N*-oxide 221  
 acid-promoted deprotection cascade reaction 150  
 acidic  $\gamma$ -caprolactamate-ligated dirhodium catalyst 151  
 $\pi$ -acidic cationic Au(I) complexes 199  
 activated alkyl electrophiles 379  
 active *N*-acyl ketiminium ions 332  
 active intermediates 25, 72, 194, 195, 322, 326, 332, 336, 349–355  
 $\alpha$ -acyl-imido sulfur ylides 144  
 acyclic 4-yn-1-ols 338  
 acyclic diene metathesis polymerization (ADMET) 243  
 3-acyloxindoles 218  
 $\alpha$ -(acyloxy)- $\beta$ -amino ketones 352  
 $\alpha$ -acyloxy carbonyl compounds 78–79, 318  
 acyl-Pd(II) species 374  
 $\alpha$ -acyl sulfur ylides 142, 144  
*Aeropyrum pernix* (*ApePgb*) 106  
 AgSbF<sub>6</sub> 285  
 alcohols 1, 56, 67, 74–76, 79, 205, 227, 229, 230, 248, 272, 287, 289, 315, 328, 331, 336, 342, 343, 358, 389, 390  
 aldehyde C(sp<sup>2</sup>)-H bond 281, 376  
 aldehydes 49, 50, 192, 193, 328, 338, 340–343, 357, 376, 377, 380, 382, 385–387  
 Aldol-addition acceptor 340, 342, 344  
 Aldol-type interception  
   ammonium ylide 340–342  
   oxonium ylide 342–343  
   zwitterionic intermediates 344  
 aliphatic amines 73, 75, 113, 340, 341  
 alkaline Al<sub>2</sub>O<sub>3</sub> 345  
 alkane functionalization 1–22  
 alkane nucleophilicity scale 18–21, 22  
 alkenes  
   intermolecular radical  
     cyclopropanation of 26–39  
   intramolecular radical  
     cyclopropanation of 39–42  
 7-alkenyl cycloheptatrienes 184, 192–193  
 7-alkenyl-1,3,5-cycloheptatrienes 178, 180  
 alkenyl cyclopropanations 184–185  
*cis*-alkenyl cyclopropanes 184  
 alkenyl sulfides 291  
 $\alpha$ -alkoxy- $\beta$ -amino acid derivatives 328  
 4-alkyl-/4-aryl-substituted enoldiazo compounds 154  
*N*-alkyl diazoacetamide 258  
 $\alpha$ -alkyl diazoacetates 31, 341  
 alkyl  $\alpha$ -diazoesters 315, 388  
 alkyl diazoacetates 31, 341  
 $\alpha$ -alkyl disubstituted diazoacetates 113  
 alkyl halides 388–390

- alkyl methacrylates 248
- alkylidene cyclopropanes 194, 195
- 8-alkylquinoline *N*-oxides 204, 227
- (*Z*)-4-alkyl-substituted enoldiazoacetates 154
- alkynals 342
- alkyne/*N*-oxide adduct 227
- alkynes 170
  - containing aryl iodides 380
  - intermolecular radical cyclopropanation of 43–44
- 1-alkynes 320–321
- alkynoate copper intermediates 349
- alkynyl diazoacetates 336
- alkynyl-containing 3,3-disubstituted oxindole derivatives 353
- alkynyl-Fischer carbenes 147
  - with 2-methylindoles 147
- alkynyl-Pd(II) species 382
- alkynylamide-substituted  $\alpha$ ,  $\beta$ -diamino acid derivatives 363–364
- alkynylaniline *N*-oxides 217
- all-*E* conjugated polyenes 193
- allene 187, 194, 375, 385
- allene-allenylcyclopropanes 194
- allenoate-Cu(I) species 322
- allenyl ketones 383
- allenyl sulfides 292
- allyl and aryl halides 373
- allylarenes 391
- allyl azides 150
- allyl diazoacetate 41, 244
- 2-allyldihydrothiophen-3-one products 201
- allyl ether 205
- allyl halides 373, 385
- allyl hydrocarbons 391
- $\pi$ -allylic palladium species 375
- allyl oxonium intermediate 205
- $\pi$ -allylPdCl 251
  - based initiating systems 253
  - based system-initiated diazoacetate polymerization 248
  - based system-initiated polymerization 246–250
    - initiated polymerization 248
- $\pi$ -allylPdCl/borate-initiated polymerization 249
- $\pi$ -allylPdCl/borate (NaBPh<sub>4</sub>) system 247
- $\pi$ -allylPdCl/borate system 250, 255–256
- $\pi$ -allylPdCl/NaBPh<sub>4</sub>-initiated polymerization 247, 250
- $\pi$ -allyl-Pd(II) species 376, 381
- [ $\pi$ -allylPd(OAc)]<sub>2</sub>-system 247
- allyl silanes 192
- allyl sulfides 291
- allyl *tert*-butyl carbonate 353, 356
- allylic selenides 309
- allylic-Pd(II) species 375, 378, 384
- allylic/propargylic sulfide 294, 302
- allylpalladium(II) 142
- alternative precursors 193
- amino acetate hydrochlorides 319
- amino acid *p*-azidophenylalanine (AzF) 124
- amino acid-derived chiral ligands 300
- 1,2-amino alcohol 340
- 3-amino-2-cyclopentenone derivatives 150
- 3-amino-2-cyclopentenone skeleton 150
- $\alpha$ -amino ester derivatives 345
- $\alpha$ -amino- $\beta$ -hydroxy acid derivatives 338
- $\alpha$ -amino- $\beta$ -hydroxyl carbonyl compounds 340
- $\beta$ -amino- $\alpha$ -alkoxyl acid derivatives 338
- syn*- $\beta$ -amino- $\alpha$ -alkoxyl acid derivatives 331
- $\beta$ -amino- $\alpha$ -hydroxyesters 331
- $\alpha$ -aminomethylation 336
- $\alpha$ -aminomethyl ether 332
- $\alpha$ -amino- $\delta$ -oxo pentanoic acid derivatives 345
- 2-aminophenol 328
- ortho*-aminophenyl imine 328
- ammonia 340, 341
- ammonium formate 358, 378
- ammonium ylide
  - Aldol-type interception 340–344
  - Mannich-type interception 327–340
  - Michael-type interception 345–349

- angularly fused tricyclic cyclopropanes 221  
 anilines 68, 70, 113, 315, 328, 339, 341, 342, 345, 355, 384  
*p*-anisaldehyde 342  
*o*-anisidine 340, 341  
 anisole/anisole-*d*<sub>5</sub> 280  
 anthracene 278  
 [4+2] annulation 236  
 [4+1]-annulation reaction 345, 394–395  
*ApePgb* W59A Y60G F145W 107  
 apo heme proteins 118  
 arene C(sp<sup>2</sup>)-H bonds 281  
 ArM (Mb-NMH) 127  
 aromatic aldehydes 340, 342  
 aromatic alkyne 107, 109  
 aromatic amines 71–73, 345  
 artificial metalloproteins (ArMs) 99, 118–125  
 aryl bromides 375, 376, 378  
 aryl carbenes 84, 85, 173, 176, 183  
 aryl chromium(0) complexes 384  
 7-aryl-1,3,5-cycloheptatriene unit 177, 183, 185, 190  
 aryl cyclopropanations 183–184  
 aryl diazoacetates 258, 322, 328, 343, 345, 363  
 α-aryl diazoacetates 322  
 α-(aryl)diazo esters 310  
 α-(aryl)diazo pyrazoleamides 310  
 aryl enynone 218  
 aryl gold(I) carbenes 174, 183, 187, 190, 191  
*N*-aryl glycine esters 332  
 aryl halides 373, 377, 378, 379, 381, 382  
*N*-aryl-imido sulfur ylides 142, 144  
 aryl iodides 373, 374, 380, 381, 384  
 β-aryl isoserine derivatives 331–332  
 2-aryl-1-naphthols 291  
 7-aryl norcaradienes 174  
 aryl substituted amino acetates 319  
 2-aryl substituted chromenes 381  
 aryl sulfoxides 202  
 aryl-linked 1,6-enynes 173  
 aryl-Pd(II) species 373, 384  
 aryl-Rh(I) intermediate 388  
 aryl-Rh(I) species 389  
 aryl-Rh(III) species 393  
 aryl-terminated ynamides 215  
 α-arylthio ester product 215  
 aryl/vinyl boronic acids 382  
 aryl/vinyl substituted α-diazo pyrazoleamides 308, 310  
 arylalkynes 227, 231  
 arylamines 327, 341, 357  
 arylboronates 388  
 aryldiazoacetates 12, 14, 345, 349  
 aryldiazoalkanes 306  
 aryl iodide 375  
 arylsiloxanes 388, 389  
 arylsulfonylprolinate ligated dirhodium(II) carboxylates 147, 148  
 arylthio ketene intermediate 215  
 α-aryl α,β-unsaturated carbonyl compounds 373  
 asymmetric catalytic [2,3]-sigmatropic rearrangements 310  
 asymmetric counter-anion-directed aminomethylation reaction 332  
 asymmetric cyclopropanation with diazosulfones 32, 34 with succinimidyl diazoacetates 31, 34  
 asymmetric Doyle–Kirmse reaction 302, 303, 308–310  
 asymmetric induction model 308, 309, 312  
 asymmetric intermolecular QC C(sp<sup>2</sup>)-H insertion reactions 283  
 asymmetric metal-catalyzed [3+2]-cycloaddition reactions 157  
 asymmetric multicomponent reactions (AMCRs) 320  
 Au(I)-catalyzed [3+2]-cyclization 150  
 Au(I)-QC intermediates 292  
 Au[<sup>t</sup>BuXPhos]Cl 161  
 axial heme-ligating residue 102  
 axially chiral biaryls 281

- axially chiral trisubstituted allenes 386
- aza*-Michael addition/ylide  
generation/intramolecular aldol  
addition 345
- aza*-Michael-and *aza*-Mannich-type  
addition 357
- azepan-4-ones 236
- azepines 158, 231, 232
- azetidin-3-ones 213
- azetidine-2,3-diones 342
- azetines 143, 144
- azides 145, 150, 387
- azodicarboxylates 328, 349, 352
- 1,3-azoles 391–392
- azomethine imines 157
- b**
- Bacillus megaterium* 96
- BB-type monomer 259
- benzamides 281, 394, 395
- benzene 90, 117, 170–172, 174, 177, 183,  
184, 194, 201, 217, 218, 224, 273,  
277
- benzene-coordinated gold(I) carbene  
177
- benzene-fused 1,5-enynes 218
- benzene-fused azepinones 217
- benzhydryl acetylene derivatives  
381–382
- (benzo)furans 281
- benzo-fused norcaradiene 174, 183, 193
- benzocyclobutenols 389
- benzofurans 106, 277
- benzophenone imine 319, 320
- benzopyrylium ions 344
- p*-benzoquinone (BQ) 373
- (benzo)thiophenes 281
- $\alpha$ -benzoyloxy propargylic esters 353
- benzyl alcohols 343, 362
- benzyl bromides 372, 383, 384
- benzyl halides 291, 372, 373, 387
- benzyl-ether-type dendron-containing  
diazooacetates 250
- benzyl-Pd(II) species 372, 373, 376, 382,  
383
- benzylamine 113, 357
- benzylic stereocenters 312
- benzylidene-ruthenium metallocarbene  
144
- B–H bond insertion reaction  
chiral Cu catalysts 88–89  
chiral rhodium catalysts 89  
enzymes 89–90
- biaryl bromides 376
- biaryl products 275, 278, 280, 281
- bicyclic cyclopropanones 221
- bicyclic diazines 156
- bicyclic pyrazolines 157
- bicyclo[1.1.0]butanes 107–108
- bicyclo[3.1.0]hex-3-en-2-ones 218
- bicyclobutane synthesis 107–108
- bicyclobutanes 107–108
- P,N*-bidentate ligand 208, 236
- P,N*-bidentate ligand Mor-DalPhos 208
- P,N*-bidentate ones 208
- bidentate phosphine ligand 215, 251
- P,S*-bidentate phosphine ligand 215
- binaphthyl-substituted Cp ligands 281
- binuclear (*R*)-(DTBM)Segphos(AuCl)<sub>2</sub>  
catalysts 149
- bioactive molecules 184, 185, 362–364
- biocatalytic carbene transfer 99, 128
- biocatalytic carbene X–H insertion  
113–118
- biocatalytic cyclopropanation 102, 104
- biotinylated dirhodium tetracarboxylate  
125
- 3,3'-bioxindole derivatives 344
- biphenyl ynone 218
- biscyclopropane 174
- bis(diazoacetate)s 264, 266
- bis(diazocarbonyl) compounds 243,  
259–266
- bis( $\alpha$ -diazo-1,3-dicarbonyl) compound  
262
- bis(diazoketone) 259, 261–263
- 2,4-bis(diazo)-1,2,3,4-  
tetrahydronaphthalene-  
1,3-dione 288
- 3,3'-bisindoles 358, 363

- 3-bisoxindoles 362  
 bisoxazoline (Box) ligands 142  
 bisoxazoline ligand 68, 70, 76, 77, 86, 87, 91, 162, 385, 386  
 bis(trimethylsilyl)diazomethanes 392  
*N*-Boc imines 352  
 bond dissociation energy (BDE) 1, 6, 14  
 Br-containing *N*-tosylhydrazones 378  
 BrettPhos ligand 292  
 bridged Mb-HMN carbenoid 127  
 bromo acylamides 375  
 2-bromobenzaldehydes 382  
*ortho*-bromo benzaldehydes 376  
 2-bromopyridine *N*-oxide 227  
 $\beta$ -bromostyrenes 381  
 Brønsted acid activation 95  
 Brønsted basicity 202  
 (*S*)-<sup>t</sup>Bu-box-Zn(OTf)<sub>2</sub> 346  
<sup>t</sup>BuBrettPhosAuNTf<sub>2</sub> 236  
 Buchner ring expansion 169, 171, 184  
 Buchner-type cyclopropanation 183  
 buta-1,3-dien-2-yl esters 150  
 butane 8, 16  
*tert*-butanol 322  
 1-butene 171  
*t*-butoxycarbonyl groups 250  
 2-(*tert*-butyl)aryl gold(I) carbenoid 191  
*N*-(*tert*-butylsulfinyl)imines 328, 332  
 3-butynol 336, 338  
 (but-3-yn-1-ylsulfinyl)benzene 201
- C**
- carbamates 69, 327, 340  
 carbazole-*p*-quinones 292  
 carbene 299  
   adducts of metalloporphyrins 99  
   insertion 3–4, 7–9, 44  
   mediated cyclopropanation reactivity 99  
   migratory insertion process 371  
   transferases 106, 113–114  
   transfer reactions with artificial metalloproteins 117–125  
   transfers 1–2, 6, 8, 14, 54–59  
 carbene–alkene metathesis product 173  
 carbene/carbenoid intermediates 205–237  
   with C–C triple bonds 224–226  
 carbene C–H insertion 109, 110, 286  
 carbene metathesis 224  
 carbene S–H insertion 113, 115  
 carbene Si/B–H insertions 115–116  
 carbene/carbenoid intermediates 1,2-C–C and 1,2-C–H insertions of 226–231  
   Friedel–Crafts reactions with arenes 215–218  
   remote C(sp<sup>3</sup>)–H functionalizations by 231–237  
   with alkenes 218–224  
   with nitrogen-based nucleophiles 212–214  
   with other heteronucleophiles 214–215  
   with oxygen-based nucleophiles 205–212  
 carbenoid adducts 175  
 carbenoid mechanistic pathways 202  
 1,2-carbonate migration approach 208  
 carbon–selenium bond 309  
 carbon–sulfur bond 309  
 carbonylation 54, 55, 374  
 $\alpha$ -carboxyone 208  
 carboxylate CO<sub>2</sub>(CH<sub>2</sub>CCl<sub>3</sub>) groups 9  
 carboxylic acids 78, 79, 107, 208, 212, 220, 281, 286, 318, 319, 393  
 carboxylic oxonium ylides 349, 352  
 cascade reactions 355–358, 374, 376, 380, 381  
 catalytic asymmetric [2,3]- and [3,3]-sigmatropic rearrangement 302  
 catalytic asymmetric Doyle–Kirmse reaction 302  
 catalytic asymmetric [2,3]-sigmatropic rearrangement reactions 302  
 catalytic promiscuity 95, 96  
 catalytic X–H insertion reactions 315  
 cationic Au(I) catalyst 201  
 cationic gold(I) catalyst 142

- C–C bond activation 371, 390  
 (±)-cermizine, C 236  
 C2-functionalized azoles 391  
 C-2 functionalized 2*H*-chromene derivatives 344  
 C–H alkylation 44  
   with acceptor/acceptor-substituted diazo compounds 45–46  
   with donor-substituted diazo compounds 46–54  
 C–H bond activation 371, 391, 393–396  
 C–H bond functionalization product 3, 396  
 CH<sub>2</sub>-carbenes 243  
 chemoselective  
   tautomerization/[2,3]-sigmatropic rearrangement reaction 291  
 chemoselectivity  
   catalysts 5–6, 8  
   catalytic systems 7  
   definition 3–4  
 C–H functionalization with carbene transferases 109–113  
 C–H insertion reactions 119, 140, 190, 286, 294  
 chiral 3-allyl-3-aryl oxindoles 353  
 chiral β-amino-α-hydroxy acid derivatives 332  
 chiral β-amino-α-hydroxy ketones 336  
 chiral α-amino-β-hydroxyphosphonates 341  
*P*-chiral biaryl phosphine oxides 281  
 α-chiral centers 113  
 chiral C<sub>2</sub>-symmetric *N,N'*-dioxide amides 300  
 chiral α,β-diamino acid derivatives 328  
 chiral 1,6-dicarbonyls 310  
 chiral 2,4-disubstituted allenates 386  
 chiral γ-nitro-α-amino-succinates 345  
 chiral *N,N'*-dioxide/Co(II) or Ni(II) catalysts 309  
 chiral *N,N'*-dioxide-metal complexes 310  
   and guanidine catalysts 299–301  
 chiral *N,N'*-dioxide amides 300  
 chiral *N,N'*-dioxide/Ni(II) complex 301, 309  
 chiral *N*-(*tert*-butylsulfinyl)imines 328  
 chiral *N*-arylsulfonylprolinate ligated dirhodium(II) carboxylates 148  
 chiral amine activated enals 349, 355  
 chiral amino thioureas 73–74  
 chiral Au catalysts 78–79  
 chiral bi-/tricyclic azines 156  
 chiral bi-/tricyclic diazines 155  
 chiral bifunctional guanidine 318, 320  
 chiral binaphthyl phosphoric acid/Rh(II) catalysts 79  
 chiral binol phosphoramidite 224  
 chiral bisoxazoline ligands 162, 386  
 chiral bisoxazoline-copper(I) complex 302  
 chiral Brønsted acids 327–329, 331, 336, 358  
   cooperative catalysis system 336  
 chiral C(sp<sup>3</sup>)—SCF<sub>3</sub> bonds 303  
 chiral carboxylic acid 281  
 chiral cationic guanidinium salts 320  
 chiral copper(I) carbene 312  
 chiral Cu catalysts  
   B–H bond insertion reaction 88–90  
   N–H bond insertion reaction 67–74  
   O–H bond insertion reaction 74–80  
   Si–H bond insertion reaction 85  
 chiral Cu(I)/bisoxazoline-catalyzed enantioselective Sommelet–Hauser rearrangement 311  
 chiral cyclopentadienyl (Cp) ligands 281  
 chiral dirhodium catalyst 14, 83, 84, 89, 341, 343  
 chiral dirhodium(II) [Rh<sub>2</sub>(*S*-PTTL)<sub>4</sub> or Rh<sub>2</sub>(*S*-PTAD)<sub>4</sub>] catalysis 155–156  
 chiral dirhodium(II) [Rh<sub>2</sub>(*S*-TCPTTL)<sub>4</sub>]-catalyzed [3+2]-cycloaddition 150  
 chiral dirhodium(II) carboxylate catalyst Rh<sub>2</sub>(*S*-BTPCP)<sub>4</sub> 161

- chiral dirhodium(II) carboxylate catalyst  
Rh<sub>2</sub>(S-PTAD)<sub>4</sub> 162
- chiral dirhodium(II) catalysts  
153, 154
- chiral dirhodium(II) complex 302
- chiral Fe catalysts 76–77
- chiral guanidine-based catalyst mediated  
asymmetric carbene insertion  
reactions 315–322
- chiral guanidine/Pd(0) complex catalyst  
315
- chiral guanidinium carboxylate 319
- chiral guanidinium salt/CuBr/YBr<sub>3</sub>  
catalytic system 321
- chiral guanidinium salts 386
- chiral ligand L<sub>2</sub>-PiPr<sub>2</sub> 311
- chiral metal catalysts 68–81, 86–87
- chiral N,N'-dioxide/metal complexes  
catalyzed rearrangement reactions  
302–315
- chiral Ni(II)/L<sub>2</sub>-Pi(OiBu)<sub>2</sub> complex 312
- chiral Ni(II)/L<sub>2</sub>-PiPr<sub>2</sub> complex 308–310
- chiral nickel carbenoid 311
- chiral nickel(II) carbenoid 308
- chiral nickel(II) catalyzed highly  
enantioselective thio-Claisen  
rearrangement 312
- chiral nickel(II) complex 308
- chiral nickel(II) directed [2,3]-sigmatropic  
rearrangement 311
- chiral nickel(II)-bonded favorable  
sulfonium ylides 311
- chiral nickel-bonded ylide intermediate  
309
- chiral organosulfur compounds 80
- chiral Pd catalysts  
N–H bond insertion reaction 69–70  
O–H bond insertion reaction 76–77
- chiral phosphoric acids 72–73, 79–80,  
95, 328, 332, 336, 338, 345, 348,  
342, 352
- chiral phthalimide-ligated  
dirhodium(II) carboxylate catalysts  
148
- chiral porphyrin ligands 28
- chiral proton-transfer shuttle (CPTS) 72  
catalysts 72, 78, 81
- chiral pyrrolidin-3-ones 213
- chiral quinine-derived squaramide 358
- chiral Rh catalysts 83–85
- chiral Rh<sub>2</sub>(S-DOSP)<sub>4</sub> 149, 310  
catalyst 310
- chiral Rh(I)-diene-catalyzed asymmetric  
three-component reaction 345
- chiral Rh(II)-or Cu(I)-based catalysts  
303
- chiral rhodium catalysts 89
- chiral Sabox ligand 142
- chiral spiro bisoxazoline ligand 68, 76,  
87, 91
- chiral sulfonium ylide 302, 311, 312
- chiral tetrasubstituted allenates 321
- chiral Zr-complex activated aldehyde  
343
- chiral/achiral Salen ligands 303
- chlorobenzene 278
- α-chloro ketone 215
- chloromethyl aryl carbenoids 176
- m*-chloroperoxybenzoic acid (*m*-CPBA)  
312
- chiral Brønsted acid synergistic catalysis  
method 346
- chroman-3-ones 218
- 2*H*-chromene products 395
- chromen-3(4*H*)-ones 226
- cinnamyl(phenyl)sulfane 308, 309
- cinnamyl(trifluoromethyl)sulfane 303
- citridin alkaloids 227
- retro*-Claisen nucleophilic ring opening  
144
- classic “privileged” chiral ligands 300
- closed shell singlet (CSS) 126
- CO 54, 99–100, 374
- Co(II)-based metalloradical carbonylation  
54
- Co(II)-based metalloradical  
cyclopropanation 32, 43
- Co(III)-carbene radicals 25
- cobalt complex 25
- (cod)PdCl(Cl-nq) 254

- (cod)PdCl(Cl-nq)/borate system 254  
collision-induced dissociation (CID) 173  
*R*-configuration sulfonium ylide 312  
conjugated enynes 379, 387  
conjugated enynones 382, 383, 385, 388, 391, 394  
*N*-containing heterocycles 51, 67, 161  
cooperative catalysis method 327, 345  
copper(I) catalyzed  
  [2+1]-cycloaddition/ring expansion 142  
copper(I)-and silver(I)-catalyzed  
  asymmetric [3+3]-cycloaddition 155  
copper(I)-vinylcarbenes 150  
copper(I)/bisoxazoline catalyst 338  
copper(II) triflate 151  
copper-catalyzed carbene cross-coupling reactions  
  coupling partners 387  
  terminal alkynes 385–387  
copper-catalyzed intramolecular cyclization reaction 338  
C1 polymerization 243–259  
cross-conjugated polymers 378  
C(sp<sup>3</sup>)-H bonds 44–54, 109–112, 236, 284, 286, 332  
  cleavage 285  
C(sp<sup>3</sup>)-H insertion 109–112, 273, 284–287, 295  
  reactions 284–286  
C(sp<sup>2</sup>)-H insertion reactions 275–284  
C-3-substituted indole 284  
  derivatives 312  
Cu(I)/bisoxazoline complexes 312  
Cu(I)/chiral bisoxazoline-catalyzed  
  Sommelet-Hauser reaction 314  
Cu(MeCN)<sub>4</sub>PF<sub>6</sub> catalyst 385, 386  
Cu-carbene 385, 391, 392  
Cu-catalyzed carbene coupling 385, 386, 392  
[Cu(CO)(tfpd)(<sup>n</sup>BuNH<sub>2</sub>)] 274  
(±)-cuspareine 110  
C-X bond forming methods 67  
cyanamides 212  
cyanide-containing pyrrolidine-2,5-diones 322  
cyclic carbonyl ylides 158  
cycloadditions 139–163, 186–189, 301, 325  
  [3+*n*]-cycloaddition 140, 154, 160  
  [3+1]-cycloaddition 141–145, 159  
  [3+2]-cycloaddition 141  
  divergent behavior of catalysts 151–152  
  with imines and indoles 145–149  
  with nitrones 150–151  
  with polarized alkenes 149–150  
  [3+3]-cycloaddition  
  with achiral catalysts 157–158  
  with diaziridines 158–159  
  with donor-acceptor cyclopropanes and oxiranes 159–160  
  with nitrones 152–155  
  with pyridinium ylides and hydrazones 155–157  
  [3+4]-cycloaddition 160–161  
  [3+5]-cycloaddition 161–162  
  (4+1)-cycloaddition 187  
  (4+3)-cycloadditions 189  
  [3+4]-cycloadducts 161  
cycloalkenylacetylenes 213  
cycloaurenones 189  
cyclobutanols 389  
cyclobutanone 205, 236  
cyclobutenes 142–144, 187  
cyclobutenyl ketones 202  
1,4-cycloheptadienes 189  
cycloheptatrienes 170, 171, 174, 177, 178–181, 183–185, 187, 189–193, 195, 196, 224  
1,3,5-cycloheptatriene 170–172, 177–185, 187, 190, 193, 195  
cyclohexane 6  
  functionalization 7  
  fused homopropargylic alcohol 205  
cyclohexyl diazoacetate (*c*-HDA) 253  
cycloisomerization reactions 140  
cyclometallation 276, 285, 286  
cyclooctadiene 254



- cyclopentadiene 187, 188  
 cyclopentane  $\beta$ -amino acids 150  
 cyclopentanone 236  
 cyclopentene 149, 150, 187  
   derivatives 149  
 3-cyclopentenyl azides 150  
 cyclopropanated  
   *N,N*-diethyl-2-phenylacrylamide  
   102  
 cyclopropanation 325  
   with acceptor-substituted diazo  
   compounds 27–34  
   with acceptor/acceptor-substituted  
   diazo compounds 32–37  
   with diverse hemeprotein carbene  
   transferases 102–109  
   with donor-substituted diazo  
   compounds 37–39  
   reactions 274  
 cyclopropanation/ring-opening cascade  
   reaction 276  
 cyclopropane 185  
   containing synthetic intermediate  
   107  
   derivatives 26  
 cyclopropane–alkene–metathesis process  
   172  
*trans*-cyclopropane 28, 96, 106  
 (1*R*,2*R*)-cyclopropanes 106  
 (1*S*,2*S*)-cyclopropanes 106  
*trans*-cyclopropanes 28, 96, 106, 183  
 cyclopropenes 43, 107, 108, 140, 163,  
   170, 343, 344, 364, 395  
   synthesis 107  
 cyclopropyl *N*-tosylhydrazones 377, 378  
 cyclopropyl diazoacetates 336  
 1-cyclopropyl-1,6-enynes 174  
 cyclopropyl ester 172  
 cyclopropyl gold carbene 185, 218  
   intermediate 218–224  
 cyclopropyl ketone product 218  
 cyclopropylalkynes 202, 204  
 cyclopropylmethyl-Pd(II) species 378  
 cyclotriphosphazene-containing  
   diazoacetates 249  
 cyclotriphosphazene-containing  
   monomers 249  
 cytochrome *c* (cyt *c*) 96  
 cytochrome *c*-catalyzed C–Si/B bond  
   formation 116  
 cytochrome P450<sub>BM3</sub> 96
- d**  
 D–A cyclobutenes and azetines 143  
 decarbenation 170  
   based on the release of alkenes  
   193–195  
   reactions from gas phase to solution  
   173  
 ( $\pm$ )-decinine 236  
 decomposition of diazo compounds 1,  
   170–171, 175, 176  
 degradative P450 enzymology 99  
 $\gamma$ -dehydro- $\alpha$ -hydroxy- $\delta$ -amino esters  
   363  
 dendron-containing diazoacetates  
   250–251  
 dendron-supported-carboxy-containing  
   poly(alkoxycarbonylmethylene)s  
   251  
 deuterium-labeling experiments  
   311–312  
 di-/tri-substituted arenes 310  
*N,N*-dialkyl aniline substrates 110  
 1,2-dialkynylbenzenes 224  
 1,1-dialkynyl carbinols 231  
 $\alpha,\beta$ -diamino derivatives 328  
 $\alpha,\beta$ -diamino ketones 352  
 $\alpha,\beta$ -diarylacrylates 372  
 $\alpha,\alpha$ -diaryl benzylic quaternary  
   stereocenter 339–340  
*cis*-1,2-diarylcyclopropanes 173  
 1,2-diaryl-1,2-diaminopropanoates 327  
*N,C*-diarylnitrones 150  
 diaryl- or triaryl-substituted cyclopropanes  
   183  
 diarylacetate products 389  
 diaryldiazomethanes 387, 392  
 diarylmethyl ethers 384  
 diastereoisomers 183

- diastereoselective [3+3]-cycloaddition
  - with achiral catalysts 157–158
- diaziridines 158–159
- 1,5-diazabicyclo[*n*.3.1]non-2-ene
  - derivatives 158
- diazoalkanes 118, 243–244, 306, 386
- $\alpha$ -diazoamides 352–353
- diazoacetamides 40, 343–344
- diazoacetates 252, 303, 328, 358
  - polymerization 249, 251
- diazoacetophenones 355
- 2-diazo-3-butenolate 150
- diazocarbonyl compounds 244, 259, 353
- $\alpha$ -diazo carbonyl compounds 89, 199, 306, 315, 373
- $\alpha$ -diazo carbonyls 83, 318–319
- $\alpha$ -diazocarboximides 158
- diazo compounds 1, 371
  - C–H alkylation
    - with acceptor/acceptor-substituted 45–46
    - with donor-substituted 46–54
  - classes of 27
  - cyclopropanation
    - with acceptor-substituted 27–34
    - with acceptor/acceptor-substituted 34–37
    - with donor-substituted 37–39
  - decomposition of 170
  - judicious selection 56
  - palladium-catalyzed cascade
    - cross-coupling reactions 374–377
    - reactions with nucleophiles 373–374
    - reactions with various electrophiles 372–373
- $\alpha$ -diazo compound 162, 302–303, 306
- diazoesters 358, 361
- $\alpha$ -diazo esters 71–73, 75, 77–78, 85, 87, 306, 308, 311, 315, 318, 321, 372, 374–376, 386, 388–390, 392–393
- diazo ester/amide 113
- diazo-functionalized five-membered
  - carbo- and heterocycles 159
- diazoketones 200, 236, 244–246, 261, 328, 336
- $\alpha$ -diazo ketones 200, 336, 373
- $\alpha$ -diazomalonates 393–394
- diazomethane 243
- diazonamide A 284
- o*-diazonaphthoquinone molecule 288
- o*-diazonaphthoquinones 278, 281, 284–291, 293
- o*-diazonaphthoquinones 285
- o*-diazonaphthoquinones 288
- 3-diazoindoles 336, 340, 341, 344, 358, 362, 363
- diazophenanthrenequinone 288
- $\alpha$ -diazophosphonates 85, 326, 341–342
- diazo pyrazoleamides 306
- $\alpha$ -diazo pyrazoleamides 303, 307–310, 312, 323
- $\alpha$ -diazo pyrrolylamide 308
- diazosulfones 32, 34
- (3-diazo-trifluorobutyl)benzene 117
- dibenzo-fused seven-or eight-membered
  - lactones 382
- dibenzo[*b,d*]thiophene 5-oxide 202
- 1,2-dibromoethane 214
- 2,6-dibromopyridine 213
- 2,5-dibromopyridine *N*-oxide 204
- 1,3-dicarbonyl compounds 190, 262, 374
- 1,2-dicarbonyl products 202, 208
- 1,2-dichloroethane 214
- 2,3-dichloronaphthoquinone 254
- 3,5-dichloropyridine byproduct 205
- dictyoptere C 189
- diene products 373, 375, 391
- 1,3-diene products 375
- 1,3,5-dienynes 218
- diflavin reductase domain 100
- 1,1-difluoroalkene 275, 387
- difluorocyclopropane analog 275
- 1,1-difluoro-2,2-diaryllkenes 388
- difluorosubstituted cyclopropane 275
- 2,3-dihydrobenzo[*b*]thiepin-4(5*H*)-one 201
- 2,3-dihydrobenzofurans 339
- dihydro- $\gamma$ -carboline 227

- dihydro-1*H*-cyclopropa[*a*]naphthalene 174  
 3,6-dihydro-2*H*-1,2-oxazines 152–155  
 3,4-dihydro-2*H*-pyran 284  
 dihydrocyclopenta[*b*]indoles 349  
 dihydrofuran-3-ones 336  
 dihydronaphthalenes 51, 53, 192  
 dihydronaphthalene 174  
 dihydronaphthofurans 289  
 dihydropyranone-fused cycloheptatrienes 224  
 1,2-dihydropyridine 231–232  
 dihydropyrroles 145, 151, 345, 355  
 2,3-dihydropyrrole 345  
 $\alpha,\beta$ -dihydroxy acid derivatives 342–343  
 1,3-diketone 263  
   products 227  
 1,4-diketone derivatives 345  
 4-(dimethylamino)pyridine (DMAP) 29, 41  
 2,3-dimethylbutane 4, 9, 12  
 1,3-dimethylindole 146  
 4-(dimethylsilyl)aniline 117  
 1,4-dioxane 261  
 1,4-dioxan-2-ones 343  
*N,N'*-dioxide  $L_2$ - $Pi(O^iPr)_2$  or  $L_3$ - $PiPr_2$  309  
 1,3-dioxo-2-gold carbenes 220  
 diphenyl sulfoxide 202, 204  
 diphenyldiazomethane 306  
 diphenylphosphate 391  
 diphenylsulfoxide 192  
 directing-group-assisted C–H bond functionalizations 393–396  
 dirhodium acetate 327, 331–332, 341  
 dirhodium catalysts 84, 276  
 dirhodium tetracarboxylate 124–125  
 dirhodium(II)  $[Rh_2(\text{cap})_4]$  catalysts 150, 156, 159  
 dirhodium(II) carbonate 319  
 dirhodium(II) carboxylates 141, 145, 147–148, 156, 161–163, 318  
 dirhodium(II) catalysis 150, 159, 162  
 dirhodium(II) catalyst  $Rh_2(S\text{-DOSP})_4$  145  
 dirhodium(II) catalysts 83, 145–146, 152–154  
 dirhodium(II)-and copper(I)-catalyzed asymmetric [3+3]-cycloaddition 153, 156  
 dirhodium(II)-enolcarbenes 161  
 dirhodium-based catalysts 15  
 dirhodium-catalyzed Aldol-type addition 340, 344  
 dirhodium/chiral Zr-complex co-catalyzed asymmetric three-component reaction 343  
 disilane 379  
 distal  $C(sp^3)$ – $C(sp^3)$  bond cleavage 389  
 distannane 379  
 1,3-disubstituted allenes 385  
 disubstituted allenates 320, 386  
 $\alpha,\beta$ -disubstituted amides 383  
*N,N*-disubstituted anilines 339  
 $\alpha$ -disubstituted carbenes 113  
 1,1-disubstituted 1,3-dienes 378  
 2,5-disubstituted 3-formylfurans 231  
 2,5-disubstituted furans 153  
 3,3-disubstituted 3-indol-3'-ylloxindoles 340  
 2,5-disubstituted oxazoles 212  
 2,4-disubstituted thiazoles 212  
 diverse P450 enzymes 102  
 divinylcyclopropane 189  
 1,2-diyne 292  
 1,5-diynes 224  
 1,6-diynes 224, 226  
 donor-acceptor  $\alpha$ -diazo pyrazoleamides 303, 323  
 donor-acceptor (D–A) cyclobutene 142  
 donor-acceptor cyclopropenes (DACPs) 140, 144, 147, 151, 154–156, 158–159, 162  
   and oxiranes 159  
 donor-acceptor-type gold carbene intermediate 215  
 double-side-armed bisoxazoline (Sabox) ligands 142

- Doyle–Kirmse rearrangement/Cope rearrangement reaction 291
- Doyle–Kirmse rearrangement/elimination reaction 291
- dual hydrogen bonding 336
- e**
- electron-deficient arenes 278–280
- electron-deficient benzaldehydes 328
- electron-donating <sup>t</sup>BuXPhos 218
- electron-poor biarylphosphonite ligand 218
- electron-rich arenes 280
- molecules 278
- electron-rich benzo-fused norcaradienes 173–174
- electronically activated ynamide moiety 220
- electronically unbiased dialkylalkynes 227
- electrophile-based enantiocontrol 336
- electrophiles 2, 18, 221, 326, 328, 332, 336, 346, 353–355, 362–364, 372–373, 377–379, 381, 385, 387, 397
- electrophilic dirhodium(II)-vinylcarbene 150–151
- electrophilic metallo-vinyl carbenes 140, 160
- electrophilic metallocarbenes 26, 29, 44, 139
- electrophilic rhodium(II)-vinylcarbenes 162
- eleutherol 285
- eleuthoside A 285
- enaldiazo compounds 357
- enals 346, 349, 355
- enamides 145, 149
- enamines 147, 345
- enantio-enriched  $\beta$ -amino lactones 111–112
- enantiodivergent C–H insertion reaction 118
- enantioenriched 3,3'-indolyloxindole derivatives 348
- enantioenriched cyclopentenones 150
- enantioenriched multifunctionalized cyclopentyl  $\beta$ -amino esters 150
- enantioenriched tertiary chiral sulfides 303
- enantioenriched tetrasubstituted allenolate 322
- enantiomerically enriched oxetan-3-ones 205
- enantioselective Diels–Alder reaction 95
- enantioselective Doyle–Kirmse reaction 303
- enantioselective Michael additions 301
- enantioselective Sommelet–Hauser reaction 310
- enantioselectivity 9–14, 31, 35, 67–68, 70, 72–78, 80–81, 83–87, 89, 91, 98, 100–101, 108–110, 114, 117–118, 125, 129, 142, 148, 151, 155, 157, 162, 281, 303, 308–311, 328, 345–346
- endocyclic vinyl carbenoid intermediate 226
- enecarbamates 150
- Z*-enecarbamate 150
- engineered heme protein-catalyzed carbene N/S–H bond insertions 115
- engineered heme protein-catalyzed heteroarene C(sp<sup>2</sup>)–H bond alkylation 114
- engineered P450 and P411 heme enzymes 98
- E*-enoldiazoacetates 144, 154
- enol ether substrates 149
- enol ethers 145, 149–150, 181, 186, 289
- enol isomer 395
- enoldiazo compounds 140–141, 151–160
- enoldiazoacetamides 147–148, 153, 161
- enoldiazoacetates 142, 144, 146, 150, 153–159, 161
- enoldiazoamides 151
- enoldiazoketones 153
- enoldiazosulfones 153–154
- enone-forming reaction 227

- enynamides 221  
 enynes 170, 173–174, 185, 218, 221, 224,  
 227, 349, 353, 379, 383, 387  
 1,6-enynes 173–174, 185, 221, 224  
 1,5-enyn-3-ol substrates 220  
 1,6-enynones 221  
 1,6-enyn-5-sulfoxides 224  
 enzymatic carbene chemistry  
   biocatalytic carbene X–H insertion  
     113–118  
   C–H functionalization with carbene  
     transferases 109–113  
   carbene transfer reactions with artificial  
     metalloproteins 118–125  
   cyclopropanation with diverse  
     hemeprotein carbene transferases  
       102–109  
   P411-catalyzed cyclopropanation  
     99–101  
   structural studies of carbene  
     intermediates in heme proteins  
       125–128  
   workflow of directed evolution  
     101–102  
 enzymatic carbene transfer 97, 107  
 enzymes 81–82, 87–91, 95–129  
   N–H bond insertion reaction 72  
 (–)-*epi*-cytoxazone 358–359  
 (4*R*,5*S*)-*epi*-cytoxazone 358  
 ethane 8, 16  
 ethyl acrylate 171  
 ethyl 2-diazobut-3-enoate 150  
 ethyl 2-diazopropanoate (Me-EDA)  
   113–114, 117, 125–126  
 ethyl C(sp<sup>3</sup>)–H bond 285  
 ethyl diazoacetate (EDA) 8, 27, 41, 97,  
   170, 253, 331, 342  
 $\gamma$ -ethyl-enoldiazoacetamide 151  
 ethyl glyoxylate 328, 338, 358  
 ethylcyclopropane 171  
 ethyldiazoacetate (EDA) 96  
 ethylene 171, 175, 194–195, 215  
 ethynylbenziodoxol(on)e (EBX)  
   353–354  
 2-ethynylphenols 338  
 5-*exo* carbonyl/6-(*endo*) carbonyl  
   products 221  
 5-*exo*-dig cyclization 84, 201, 382  
*exo*-double bonds 380  
 external nitrogen-/carbon-based  
   nucleophiles 376  
 external sulfoxides 202
- f**
- facile gold-catalyzed intermolecular  
   alkyne oxidation 218  
 F-containing C1 polymers 258  
 F-containing  
   poly(aryloxy-carbonylmethylene)  
     259  
 Fe(II)–CO complex 100  
 Fe(III) porphyrin complexes 127  
 Fe(OTf)<sub>3</sub> 277  
 Fe(TPP)(CCL<sub>2</sub>)(H<sub>2</sub>O) complex 99  
 F–H bond insertion reaction 82–83  
   enzymes 82  
 five-membered sulfonium salt 201  
 five-membered-palladacycle 375  
 flavonones 384  
 fluorene derivatives 376  
 fluorinated diazo compounds 328  
 fluorinated dihydroisoxazoles 353  
 fluorine-containing aryl groups 258  
 fluoroalkyl and fluoroaryl  
   group-containing polymers  
     258–259  
 fluoroaryl diazoacetates 258  
 fluoro-benziodoxole 353, 355  
 $\alpha$ -fluoro ketones 215  
 (–)-Folicanthine 358, 360  
 formaldehyde 259, 340, 344  
 formaldimines 336  
   precursors 161  
 Friedel–Crafts reactions of  
   carbene/carbenoid intermediates  
     with arenes 215–218  
 Friedel–Crafts-type cyclization 188, 201  
 fully substituted tetrahydrofurans 346,  
   348  
 functionalized 3-amino oxindoles 342

- functionalized azepines 231, 232  
 functionalized  
   spiro-chroman-4,3'-oxindole  
   derivatives 344  
 furan-containing olefins 382  
 furan-containing triarylmethanes 388  
 furan-substituted 1,3-dienes 391  
 furan-substituted olefins 382  
 furans 56, 185–187, 277, 281, 355  
 furyl- and vinyl diazo compounds 140  
 furyl-substituted isoindolinones 394  
 fused indolines 145
- g**
- gas-phase decarbenation 173  
 gaseous alkanes 14–17  
*gem*-difunctionalization of metal carbene  
 species 326, 357  
*gem*-difunctionalization products 353  
*gem*-disilylated oxazoles 392  
 geminal bis(silane) 379  
 geminal bis(stannane) 379  
*in situ* generated ammonium ylide 328,  
 341  
*in situ* generated iminoesters 340  
 glass transition temperature 264  
 gold-activated alkynes attacked by  
   nucleophilic oxidants 199, 200  
 gold alkenylcarbene species 150  
 gold carbene intermediates 205, 212,  
 215, 218  
 gold carbenoid 177, 201  
 gold(I) carbene 174, 177, 179, 183–185,  
 187–188, 190–191, 193  
   complexes 173  
 gold(I)-catalyzed methylenecyclopropane-  
 cyclobutene rearrangement 187  
 gold(I)-catalyzed one-pot [2+2]  
   cycloaddition 187  
 gold(I)-catalyzed retro-Buchner reaction  
 173–176  
 gold(I)/chiral phosphoric acid cooperative  
 catalysis 336  
 gold(I) chloromethyl carbenoid 176  
 gold(I)-coordinated norcaradiene 178  
 gold(I) phosphonium ylides 173  
 gold-catalysis  
   *N*-oxides as nucleophilic oxidants  
     202–237  
   gold-activated alkynes attacked by  
     nucleophilic oxidants 199, 200  
     sulfoxides as nucleophilic oxidants  
       201–202  
 gold-catalyzed intermolecular  
   oxoarylation 202  
   of alkynes 203  
 gold-catalyzed intramolecular alkyne  
   oxidation 217  
 gold-catalyzed oxidative cyclizations 221  
 gold-enolcarbenes 161  
 gold-vinylcarbenes 161  
 $\beta$ -gold vinyl cation intermediate 224, 226  
 guanidine 70, 78–79, 299–323, 345  
 guanidine-amide catalysts 301  
 guanidine-amides 300–301, 322, 323
- h**
- $\alpha$ -halogenated ketones 214  
 H-atom abstraction and radical  
   substitution (HAA-RS) 45, 49  
 hazardous diazo carbonyl compounds  
 204, 238  
 $2\text{H}^+ / 2\text{e}^-$  ferraquinone/ferrahydroquinone  
 redox couple 272  
 $1\text{H}^+ / 1\text{e}^-$  Ru(II)-QC/Ru(III)-aryl couple  
 273  
 heme domain 100  
 heme proteins 96, 99, 102  
   carbene transferases 112, 113  
 hemoglobin 96  
*N*-heteroarene *N*-oxides 204  
 heteroaromatics 280  
 heteroaryl bromides 376, 378  
 heteroatom-hydrogen (X–H) bonds 67,  
 315  
   B–H bond insertion reaction  
     chiral Cu catalysts 88–89  
     chiral rhodium catalysts 89  
     enzymes 89–90  
   F–H bond insertion reaction 82–83

- insertion reaction 67
- N–H bond insertion reaction 67
- amines 73
  - chiral amino thioureas 73–74
  - chiral Cu catalysts 68–70
  - chiral Pd catalysts 70
  - chiral phosphoric acids 72–73
  - chiral proton-transfer shuttle catalysts 72
  - enzymes 72
- O–H bond insertion reaction 74
- chiral Au catalysts 78
  - chiral Cu catalysts 74–76
  - chiral Fe catalysts 76–77
  - chiral Pd catalysts 77–78
  - chiral phosphoric acids 79–80
  - CPTS catalysts 78–79
- S–H bond insertion reaction 80
- chiral metal catalysts 80–81
  - CPTS catalysts 81
  - enzymes 81–82
- Si–H bond insertion reaction 83
- chiral Cu catalysts 85–86
  - chiral metal catalysts 86–87
  - chiral Rh catalysts 83–85
  - enzymes 87–88
- heterocyclic imines 332
- 3-heterocyclic motif substituted
- 3-hydroxyoxindoles 343
- heterogenous, immobilized enzyme preparation 101
- hexamethylbenzene 171
- hexamethylnorcaradiene 171
- n*-hexyl diazoacetate 249
- higher formal cycloaddition 169, 186–189
- highly strained bicyclobutanes 172
- highly substituted indanol derivatives 389
- histidine (C400H) 101
- HO-containing C1 polymers 255
- homoallylic–Pd(II) species 378
- homodimeric LmrR 122
- homopropargyl alcohols 343
- horseradish peroxidase (HRP) 96
- H–Pd(II) species 374, 378
- hydrazones 46, 54, 70, 155–157
- hydrogen atom transfer (HAT) 114, 127, 273, 286
- hydrogen-activated isatin 322
- hydrosilanes 384
- hydroxy group-containing polymers 254–256
- hydroxy-containing poly[alkyl (meth)acrylate]s 254–255
- hydroxy-containing vinyl polymers 255
- hydroxydiynes 174
- $\delta$ -hydroxyketone derivatives 346
- $\gamma$ -hydroxyl carbene intermediate 343
- $\beta$ -hydroxyl- $\alpha$ -amino acid derivatives 332
- $\alpha$ -hydroxyl- $\delta$ -amino ester derivatives 362
- $\beta$ -hydroxy- $\alpha$ -amino phosphonates 341
- 3-hydroxyoxindole moieties 358
- hypervalent iodine reagents 353
- i**
- imines 56, 145–152, 157, 327–332, 334, 338–340, 345, 352–353, 355, 358, 363
- 2-iminyl 2-acyl-substituted phenols 339
- InBr<sub>3</sub> 342
- indane-1,2,3-triones 342
- $\alpha$ -indanones 394
- indenecarboxamide 221
- indenofuranone 224
- indenone 224
- indole-*p*-quinones 292
- indoles 277, 281, 358
- indole alkaloids 358
  - indole/ketal derived iminiums 346
- indolines 46–48, 50, 145, 341, 355
- indolizinone product 208
- indolones 341
- 2-indolylmethanol derived delocalized cations 346
- insertion reactions 67–90, 190–192, 275–286, 299–323
- intermediate gold(I) carbene 183

- intermolecular 1,2-proton transfer process 319
- intermolecular 1,3-proton transfer process 311
- intermolecular C(sp<sup>2</sup>)-H insertion product 277
- internal aliphatic alkynes 109
- internal alkynes as the coupling products 386–387
- intramolecular Aldol-type transformations 343, 345
- intramolecular alkene carbopalladation 375
- intramolecular carbene O–H insertion 205
- intramolecular cyclopropanation 40–42, 104, 106, 275
- intramolecular Friedel–Crafts reactivity 190
- intramolecular transformations 1
- 2-iodoanilines 384
- 2-iodophenols 384
- Ir(Me)-CYP enzyme 118
- Ir(Me)-reconstituted ArMs 120
- Ir(Me)-substituted myoglobins 119
- Ir-catalyzed aryl C–H bond alkylation 393
- iridium(I)-associated zwitterionic intermediate 349
- iridium(III) porphyrin-catalyzed intermolecular QC C(sp<sup>3</sup>)-H insertion reaction 286
- iron catalyst 8, 107, 109–110
- iron porphyrin catalyst Fe(TPP)Cl 340
- iron-2,4-diacetyl deuteroporphyrin (Fe-DADP)-substituted myoglobin 119
- iron-based catalysts 109
- iron-carbene precursors 110
- iron-catalyzed three-component reaction 341
- iron-deuteroporphyrin (Fe-DPIX) 119
- iron-porphyrin carbene (IPC) 125
- iron-phthalocyanine catalyst 109
- isatins 321, 340, 342, 343, 358
- and pyrazolinone-derived ketimines 332
- derived ketimines 340
- ketimines 352
- isocoumarin derivatives 376
- isoindolinone derivatives 332
- isoindolone derivatives 394
- isoquinolines 395
- isoquinolinium dicyano-/dicarbomethoxy-methylides 156
- 8-isopropylquinoline *N*-oxide 215, 227
- 5-isoxazolones 151
- j**
- Julia–Kocienski olefination 180, 193
- k**
- N,S*-ketals 349
- ketene imines 145, 149–150
- β-ketoaldehyde intermediate 227
- β-keto enol ether framework 263
- α-ketoesters 340, 342
- keto-iminium 346
- kinetic isotope effect (KIE) 110, 127, 215, 280, 285
- kosinostatin aglycone 289, 292
- l**
- β-lactam derivatives 342
- lactococcal multidrug resistance regulator (LmrR) 122
- lactone products 277, 281, 382
- lactone-based carbene 111
- lactone-based organoboron compounds 117
- lasubine II, 236
- late transition metal catalyzed ene-yne-ketone 140
- laurokamurene B 188
- (±)-laurokamurene B 188
- (+)-lentiginosine 236
- levomilnacipran 102
- Lewis acid [Yb(OTf)<sub>3</sub>] 159
- Lewis acid/rhodium-catalyzed formal [3+3]-cycloaddition 159



- Lewis acidic copper(II) triflate 151  
 Lewis acids 159, 199, 243, 250, 338, 342  
 Lewis-acid-bonded ylide pathway 308–309  
 (+)-lyngbic acid 110
- m**
- Mannich reaction 95  
 Mannich-type interception  
 ammonium ylide 327  
 oxonium ylide 328–339  
 zwitterionic intermediates 339–340  
 Me-DalPhos 208  
 Me<sub>4</sub>NSCF<sub>3</sub> 387  
 6-membered cyclic ether 261  
 7-membered nitrilium intermediate 212  
 mesitylene 171, 181, 184, 185  
 α-mesyloxy ketones 212  
 metal-bonded ylide 302, 303  
 metal carbene cycloaddition reactions  
 [3+1]-cycloaddition 142–145  
 [3+2]-cycloaddition 145–152  
 [3+3]-cycloaddition of enoldiazo  
 compounds 152–160  
 [3+4]-cycloaddition 160–161  
 [3+5]-cycloaddition 161–162  
 “metal carbene radical” intermediates 286  
 metal carbenes 1, 325  
 alkenyl cyclopropanations 184–185  
 alternative precursors 193  
 aryl cyclopropanations 183–184  
 decarbenation 170–171  
 decarbenations based on the release of  
 alkenes 193–195  
 insertion reactions 190–192  
 intramolecular Friedel–Crafts reactivity 190  
 metal-catalyzed decarbenations 175–181  
 oxidation reactions 192–193  
 reactions with furans 185–186  
 reactivity and generation of 169–171  
 retro-cyclopropanation reactions 171–175  
 species 371  
 metal–carbenoids 299–323  
 metal-catalyzed decarbenation 169–196  
 metal-free ylide intermediate 343  
 “metalloalkyl radicals” 286  
 metallo-enolcarbenes 140, 141, 144, 147, 150  
 sources 148  
 (*E*)-metallo-enolcarbene 159  
 15e-metalloradicals 25  
 metal-porphyrin-carbene species 99  
 metal-quinoid carbene (QC) complexes  
 C(sp<sup>2</sup>)-H insertion reactions 275–284  
 C(sp<sup>3</sup>)-H insertion reactions 284–286  
 cyclopropanation reactions 273–275  
 nucleophilic addition and  
 miscellaneous reactions 286–293  
 metallo-vinyl carbenes 140, 141, 145, 146, 148, 149, 151, 157, 160, 161  
 precursors 140  
 metallo-vinylcarbene/cyclopropene/  
 vinyl diazo compound connectivity 140  
 metallocarbenes 44, 139, 142, 146, 160  
 intermediates 3  
 metalloporphyrin analogs 98  
 metalloradical catalysis (MRC) 25–60  
 metalloradicals 25, 139  
 methane 8, 14–19, 22, 84, 99  
 methanesulfonyloxymethyl ketones 212  
 methanofullerene derivatives 172  
*p*-methoxybenzyl methyl ether 110  
 methyl phenyldiazoacetate 327  
 methylated carbene precursors 180  
 2-methyl-5-bromopyridine byproduct 205  
 1-methylcyclohexene 286  
 3-methylcyclohexene 286  
 methylene iminium ions 340  
 methylenecyclopropanes 187  
 N<sub>5</sub>-methylhistidine 127  
*N*-methylindole nucleophiles 145  
 8-methylquinoline *N*-oxide 204, 208, 214, 220, 224, 285, 383  
 8-methylquinolines 285

- N*-methyl tetrahydroquinoline 110  
 Michael-type interception  
     ammonium ylide 345–346  
     oxonium ylide 346–348  
     zwitterionic intermediate 348–349  
 $M_n$  polymers 245–246  
 [Mo(CO)<sub>6</sub>] 274  
 molybdenum-based catalytic system 193  
 mono and bicyclic chiral guanidines 301  
 Mor-DalPhos 208, 212, 215, 220  
 Morita-Baylis-Hillman (MBH) carbonates 349  
 morpholine 113  
 multi-component reactions (MCRs) 325–327, 358, 362, 364  
 multi-substituted allenes 385–386  
 multi-substituted dienes 375, 380  
 multi-substituted phenols 291  
 multi-substituted pyrrolidines 355  
 multifarious chiral catalysts systems 302  
 multifunctionalized 5-isoxazolones 151  
 multiple site targeting 102  
 myoglobin (Mb) 96, 106, 112  
 myriad oxidative chemistry 96
- n**
- NaBPh<sub>4</sub> [(cod)PdCl(Cl-nq)/borate system] 254  
 NaBPh<sub>4</sub> [(nq)<sub>2</sub>Pd/borate system] polymerized diazoacetates 251  
 naphthalene 171, 174–175, 193–194, 288  
     derivatives 396  
 1,2-naphthalenediol 285  
 1,2-naphthalenediol derivatives 287  
 1,2-naphthalenediol diacetates 288  
 1,2-naphthalenediol monoacetates 287  
 naphthoquinone (nq) 251  
     -ligated zero valent Pd complex 245  
*p*-naphthoquinones 292  
 7-naphthyl-1,3,5-cycloheptatriene 187  
 α-naphthyl esters 289  
 natural alkaloid (±)-gliocladin C 358  
 natural fatty acid lactobacillic acid 185  
 natural products 40, 44, 110, 118, 181, 188, 195, 231, 238, 277, 289, 323, 358–362  
 navenones 193  
 Nazarov-type cyclization 212  
 N–H bond insertion reaction  
     chiral amino thioureas 73–74  
     chiral Cu catalysts 68–70  
     chiral Pd catalysts 70  
     chiral phosphoric acids 72–73  
     chiral proton-transfer shuttle catalysts 72  
     enzymes 72  
 (NHC)Pd(nq)/borate-initiated polymerization 245–246  
 (NHC)Pd(nq)/borate system 245–246, 253  
*N*-heterocyclic carbene (NHC) 8, 90, 117, 221, 245–246, 253  
     stabilized borane 117  
 N–H insertion process 315  
 Ni(BF<sub>4</sub>)<sub>2</sub>/L<sub>2</sub>-Pi(O<sup>*i*</sup>Bu)<sub>2</sub> 312  
 Ni(II)/L<sub>2</sub>-PiPr<sub>2</sub> complex 308–310  
 NiBr<sub>2</sub>-/CoBr<sub>2</sub>-catalyzed C2-alkylation 392  
 β-nitroacrylates 345–346  
 2-nitrobenzaldehyde 340–341  
 nitroenynes 349  
 nitrones 150–155, 158, 160, 204, 271, 284, 291, 336, 338  
 nitrosoarenes 151–152, 271, 291, 353  
 non-acceptor diazo compounds 170  
 non-acceptor rhodium(II) carbenes 180  
 non-acceptor vinyl rhodium(II) carbenes 189  
 non-arene-fused 1,6-diyne 226  
 non-conjugated dienes 243  
 non-diazo carbene precursors 336, 343, 364  
 non-directing-group-assisted C–H functionalizations 391–392  
 non-heme protein scaffolds 118, 124  
 non-porphyrin organometallic moieties 118  
 norbornene (NBE) 380

- norcaradiene 150  
 intermediate 224  
 tautomer 171  
 (nq)<sub>2</sub>Pd/borate-and  
 (cod)PdCl(Cl-nq)/borate-initiated  
 polymerization 251  
 (nq)<sub>2</sub>Pd/borate-initiated polymerization  
 253  
 (nq)<sub>2</sub>Pd/borate system 253  
 nucleophiles 373, 379  
 functionalization, catalytic cycle 2  
 nucleophilic addition and miscellaneous  
 reactions 286–293  
 nucleophilic metal carbenes 139
- O**
- O–H insertion product 342  
 O–H bond insertion reaction 74  
 chiral Au catalysts 78  
 chiral Cu catalysts 74–76  
 chiral Fe catalysts 76–77  
 chiral Pd catalysts 77  
 chiral phosphoric acids 79–80  
 CPTS catalysts 78–79  
 olefin cyclopropanation 26, 27, 29, 32,  
 34, 35, 37, 39, 102, 104, 128  
 oligo(oxyethylene)-containing polymers  
 256–257  
 one-pot formal [3+3]-cycloaddition  
 159  
 open shell singlet (OSS) 126, 127  
 Oppolzer's camphor sultam auxiliary and  
 Cu(I) catalyst 303  
 optically active β-amino-α-hydroxyl acid  
 derivatives 358  
 optically active 3,3'-bisindoles 358  
 optically active α-hydroxyl-β-amino acids  
 332  
 optically active selenides 309  
 optically active sulfur-containing  
 molecules 302  
 organoboronic acids 373, 383  
 organocatalysts 300  
 organocopper species 353, 385, 387  
 organocopper(I) species 387  
 organometallic species 176, 371, 394  
 organostannanyl reagents 389  
 ortho-alkenyl phenol products 393  
 osmium vinylidenes 195  
 oxa-π-allylrhodium complex 388  
 oxacyclic ketone products 205  
 1,3-oxazin-4-ones 151  
 oxetan-3-one 213  
 oxetane 288  
 oxidation reactions 192–193  
 oxidative 1,5-enyne cyclopropanation  
 220  
 oxidative addition 254, 371, 372, 375,  
 378, 379, 382, 383  
 oxidative gold catalysis 199, 201, 202,  
 204, 215, 218, 227  
 oxidative transmetalation 245, 253  
 N-oxides as nucleophilic oxidants  
 202–237  
 oximes 393, 395, 396  
 oxindole-derived α-alkoxy-β-amino acids  
 332  
 oxindoles 342, 348, 353, 362  
 oxiranes 159  
 α-oxo gold carbene (T) 199, 201, 205,  
 208  
 intermediates 199, 205, 215, 236  
 regioisomer 231  
 4-(2-oxoindolin-3-yl)-1,4-dihydropyridines  
 349  
 oxonium ylide 288  
 Aldol-type interception 342  
 Mannich-type interception 328  
 Michael-type interception 345–349  
 oxonium ylide species 287  
 oxyethylene-containing  
 poly(alkoxycarbonylmethylene)s  
 256  
 oxygen-binding heme protein 106
- P**
- “paddlewheel” dirhodium compounds  
 151  
 palladacycle 375, 376, 382  
 palladacycle species 376

- palladium catalysis 157
- palladium(II)/chiral phosphoric acid
  - catalyzed three-component reaction 345
- palladium-catalyzed carbene
  - cross-coupling reactions
  - N*-tosylhydrazones 377–382
  - diazo compounds 372–377
  - non-diazo compounds 382–385
- palladium-catalyzed cascade
  - cross-coupling reactions 374–377, 380–382
- palladium/phosphoric acid (PA\*)
  - complex 346
- P411<sub>BM3</sub>-CIS 101, 105, 106
- P411-catalyzed cyclopropanation 99–101
- Pd<sub>2</sub>(dba)<sub>3</sub>(CHCl<sub>3</sub>) 254
- Pd(0) complex 253, 254, 315
- Pd(II)-catalyzed QC reaction 288
- Pd(OAc)<sub>2</sub> 172, 287, 288, 291
- Pd(OAc)<sub>2</sub>-catalyzed intermolecular QC
  - O–H insertion 287
- Pd-based initiating systems 244
- Pd-carbene 247, 318, 373–375, 378–385
- Pd-carbene migratory insertion 378–381
- Pd-catalyzed C(sp<sup>3</sup>)-H bond activation 375
- Pd-catalyzed carbene coupling reactions 378
- Pd-catalyzed Si–H bond carbene
  - insertions 379
- PdCl<sub>2</sub>-based initiating system 244
- PdCl<sub>2</sub>-based system 245
- PdCl<sub>2</sub>-initiated polymerization 244–245
  - of diazoketones 245
- pentafluoro diazopropane 110
- P450<sub>BM3</sub> enzymes 102
- P450 enzymology 99
- peroxidase YfeX and P411s 112
- Ph<sub>3</sub>PAuNTf<sub>2</sub> 227
- phenanthrene 193
  - derivatives 172
- 9,10-phenanthrenedioxycetals 288
- 1,10-phenanthroline 392
- N*-phenoxyacetamides 393–395
- phenoxyethynes 338
- α-phenoxy ketones 344
- 2-F-phenyl and 2,6-F<sub>2</sub>-phenyl
  - diazoacetates 258
- 1-phenylbutyne 109
- 4-phenylbutyne 107
- phenyldiazoacetate 327, 340, 341
- phenylhydrazones 156
- N*-phenylmaleimides 322
- (–)-8-phenylmenthol 147
- 3-phenylpropanoic acid 310
- N*-phenylpropiolamides 218
- (*Z*)-4-phenyl-substituted
  - enoldiazoacetates 155
- N*-pivaloyloxy benzamides 394–395
- phosphazene-containing diazoacetates 249, 250
- phosphoramidates 328
- phosphorus ylides 144
- phthalimide-alanine ligated Rh<sub>2</sub>(*S*-PTA)<sub>4</sub> catalyst 152
- phthalimide-amino acid ligands 156
- PhWCl<sub>3</sub>-EtAlCl<sub>2</sub> pair 171
- pincer-type Ru-and Fe-QC complexes 271
- pivalic acid 285
- P450 monooxygenase mutants 100
- polarized alkenes 145, 149–150
- poly(2-hydroxyethyl methacrylate)
  - [poly(2-HEMA)] 255
- poly(2-hydroxypropyl acrylate)
  - [poly(2-HPA)] 255
- poly(β-keto enol ether)s 263
- poly(*N*-alkylacrylamide)s 259
- poly(*N*-alkylcarbamoylmethylene)s 259
- poly(*N*-isopropylacrylamide) 259
- poly(alkoxycarbonylmethylene) 244, 251, 254–258
- poly(alkyl acrylate)s 254, 256
- poly(alkyl methacrylate)s 256
- poly(alkylmethylene)s 243
- poly(allyloxycarbonylmethylene) 244
- poly(arylene vinylene) (PAV) synthesis 265

- poly(arylene-1,1-vinylidene)s (*iso*-PAVs) 378
- poly-substituted alkenes 377
- poly-substituted indanes 375
- polyamines 264
- polyfluoroarenes 392
- polyfunctionalized furans 56
- polyfunctionalized indole derivatives 339
- polyhalogenated methane xenobiotics 98–99
- polymethylene 243
- polysubstituted 1,3-dienes 373
- porphycene-modified myoglobin 127
- powerful nucleophiles 1
- $\text{PPh}_3\text{AuNTf}_2$  214
- pradimicinone 277
- primary alkyl groups 245
- prolyl oligopeptidase (POP)-based ArM 124
- promiscuous P411 enzyme 107
- propane 16, 17
- propargyl alcohol 287
- tert*-propargyl alcohols 389–390
- propargyl aryl ethers 218
- propargyl carboxylates 170
- propargyl esters 157
- propargyl sulfides 292, 303
- propargyl-Cu(I) species 386, 387
- propargylic alcohol 205
- propargylic esters 150, 353
- propargylic sulfonamides 213
- propiolamides 218, 363
- proteins 95–100, 103, 106, 113, 118, 119, 125–128
- protic carbamate ammonium ylides 327
- 1,3-proton transfer process 310–312
- proximal ligand 102
- P411 variant P4-A82L 110
- P411-VAC<sub>cis</sub> 106, 107
- P411-VAC<sub>trans</sub> 106
- pyrazole 162, 280, 303
- pyrazoleamide group 303, 308
- pyrazoleamide unit 306, 308
- pyrazolone derivatives 332
- pyrene-containing diazoacetates 257
- pyrene-containing polymers 257–258
- pyridine *N*-oxides 204, 395
- pyridines 204, 244, 280, 393
- N*-(pyridine-2-yl)- $\epsilon$ -lactams 212
- pyridinium ylides 155–157
- pyridinium zwitterions 161, 162
- pyrido[2,1-*a*]isoindoles 194
- pyridotriazoles 336
- pyrimidine 280
- pyrroles 42, 113, 277, 281, 339
- $\alpha$ -pyrrolylbenzylamines 357
- q**
- QC C(sp<sup>2</sup>)-H insertion reactions 275, 277–284
- Q-DEAN (Quantitative DEscriptor-based Alkane Nucleophilicity) 18, 22
- o*-QM via H-bonding 348
- quaternary  $\alpha,\alpha$ -diaryl carboxylic esters 388
- p*- and *o*-quinone diazides 275, 278–281, 284, 286, 291–292
- quinoid-aromatic tautomerism 272
- quinolines 204
- diazides 278
- N*-oxide 292
- ortho*-quinone methide (*o*-QM) 346
- p*-quinone products 292
- r**
- radical olefin cyclopropanation 26
- radicals 25
- rapamycin 358, 361–362
- reaction pathways of multi-component reactions 326
- reactions with furans 185–186
- reactive  $\beta$ -gold vinyl cation intermediate AT 224
- reactive Pd-carbene intermediate 318
- rearrangement reactions 291, 294, 301–315
- recombinational cloning 102

- regiodivergent copper(I)- and rhodium(II)-catalyzed [3+3]- versus [3+2]-cycloadditions 158
- regioselective C(sp<sup>2</sup>)-H alkylation of pyrroles 113
- regioselective C-H functionalization 280
- regioselectivity 8  
catalysts 5-6  
definition 3-4
- remote C(sp<sup>3</sup>)-H functionalizations by carbene/carbenoid intermediates 231-237
- retro-Buchner reaction 170-171, 173-177
- retro-Buchner/retro-cyclopropanation 170
- retro-cyclopropanation reactions 171  
decarbenation reactions from gas phase to solution 173  
early observations 171-172  
gold(I)-catalyzed retro-Buchner reaction 173-175
- reversible NaOAc-facilitated *aza*-aldol process 355
- reversible water-assisted 1,3-proton transfer process 312
- Rh<sub>2</sub>-catalytic systems 43
- [Rh<sub>2</sub>(esp)<sub>2</sub>]-catalyzed cyclopropanation reaction 284
- [Rh<sub>2</sub>(esp)<sub>2</sub>]-catalyzed intermolecular cyclopropanation 275
- Rh<sub>2</sub>(S-MSP)<sub>4</sub> 147
- Rh<sub>2</sub>(OAc)<sub>4</sub> 260, 318, 327, 346  
catalyzed three-component reaction 363  
catalyzed three-component tandem 1,4-conjugate addition-cyclization reaction 355  
catalyzed Mannich-type addition 352  
catalyzed two component polycondensation 262
- [Rh<sub>2</sub>(OAc)<sub>4</sub>] 284, 287
- [Rh<sub>2</sub>(OAc)<sub>4</sub>]-catalyzed intramolecular QC C(sp<sup>3</sup>)-H insertion 285
- [Rh<sub>2</sub>(OAc)<sub>4</sub>]-catalyzed intramolecular QC transfer 275
- [Rh<sub>2</sub>(OAc)<sub>4</sub>]-catalyzed QC reaction 288
- Rh<sub>2</sub>(OAc)<sub>4</sub>/chiral Brønsted acid co-catalyzed three-component reactions 358
- [Rh<sub>2</sub>(OCOCF<sub>3</sub>)<sub>4</sub>] 277
- Rh<sub>2</sub>(S-PTAD)<sub>4</sub> 149, 156, 162, 341
- Rh<sub>2</sub>(S-PTIL)<sub>4</sub> 156
- Rh<sub>2</sub>(S-PTTL)<sub>4</sub> 151, 156, 341
- Rh(I) precatalysts 281
- Rh(I)-associated ammonium ylides 345
- Rh(I)-chiral diene complex 85, 341
- Rh(III)-catalyzed asymmetric [4+1] annulation 394
- Rh(III)-catalyzed intermolecular QC C(sp<sup>3</sup>)-H insertion 285
- Rh- and Ir-catalyzed intermolecular QC C(sp<sup>2</sup>)-H insertion reaction 280, 282
- Rh-carbene 394
- Rh-carbene species 319, 388-390, 393
- Rh-catalyzed intermolecular QC C(sp<sup>2</sup>)-H insertion reaction 277, 279
- Rh-catalyzed intermolecular QC C(sp<sup>3</sup>)-H insertion reaction 286
- Rh-catalyzed intermolecular QC cyclopropanation reaction 276
- Rh/Chiral Zr-complex Co-catalyzed asymmetric three-component reaction 343
- [Rh(cod)<sub>2</sub>OTf] 390
- rhodacycle 395
- rhodacyclic species 393
- rhodium acetate 151, 327, 331-332, 341
- rhodium porphyrin (TPP)RhI 97
- rhodium(II) acetate 142, 155
- rhodium(II) octanoate 150-151
- rhodium(II) octanoate [Rh<sub>2</sub>(oct)<sub>4</sub>] catalyzed [3+2]-cyclization 150
- rhodium(II)-catalyzed decarbenation 181
- rhodium(II)/chiral Brønsted acid cooperative asymmetric catalytic three-component reaction 341

- rhodium-catalyzed Aldol-and Mannich-type interception reactions 352
- rhodium-catalyzed carbene cross-coupling reactions 388–390
- rhodium-catalyzed novel *gem*-difunctionalization 353
- rhodium-containing organometallic complexes 124
- rhodium-enolcarbene 150
- rhodium-porphyrin [Rh(D<sub>4</sub>-por\*)(Me)(MeOH)] complex 12
- rhodium-vinylcarbenes 145
- rhodium/chiral phosphoric acid cooperative catalysis 336, 338
- rhodium/piperidine relay catalysis 348
- Rhodothermus marinus* (*Rma*NOD) 106, 107
- [Rh<sub>2</sub>(OPiv)<sub>4</sub>] 277
- [Rh<sub>2</sub>](TFA)<sub>4</sub>, vinylogous aldehydes 193
- ring-opened THF 247–248, 250, 260–262
- ring-opening metathesis polymerization (ROMP) 243
- Rma* cyt *c* 87–88, 114–117
- Rma* cyt *c* borylases 117
- Rma* cyt *c* V75R M100D M103T 117
- Rma* cytochrome *c* variant (*Rma* TDE) 125–127
- Rma*NOD Q52V 107
- Ru(II) porphyrin QC complexes 270–271
- Ru(II) porphyrins 270, 291
- Ru(II)-associated ammonium ylides 355
- Ru-catalyzed polymerization 264
- Ru/Pd-co-catalyzed asymmetric allylic alkylation 353
- ruthenium catalysts 264
- S**
- Sabox ligand 142, 153, 156
- salicylaldehyde derived *N*-tosylhydrazones 381
- s-cis* styrylcarbene 146
- second-generation cycloheptatrienes 179–181
- secondary propargylic alcohols 205, 230
- selective carbene transfer processes 26
- selectivity, control of 21
- Ser-ligated P411 enzymes 102
- serine-ligated enzymes 100, 101
- seven-membered carbocycles 161
- [2,3]-sigmatropic rearrangement 201, 205, 312
- of sulfonium ylide 308
- process 311
- reactions 302
- [3,3]-sigmatropic rearrangement 150, 201, 302, 315, 323
- S–H bond insertion reaction 80
- chiral metal catalysts 80–81
- CPTS catalysts 81
- enzymes 81–82
- Si–H bond insertion reaction 83
- chiral Cu catalysts 85–86
- chiral metal catalysts 86–87
- chiral Rh catalysts 83–85
- enzymes 87–88
- Si–H insertion 110, 114, 115, 117, 119, 126, 127, 192
- silane-containing naphthyl bromides 380, 381
- 2-siloxy-substituted cyclobutene-1-carboxylate 142
- silver(I) salts 142
- silyl-protected enoldiazoacetates 142, 144, 159
- silyl-protected metallo-enolcarbene 141
- silyl-protected monomers 256
- silylketenes 231, 234
- single component polycondensation
- of bis(diazocarbonyl) compound to afford poly(arylene vinylene)s (PAV) 265–266
- of bis(diazocarbonyl) compound to afford unsaturated polyesters 264–265
- six-membered  $\beta$ -phenylnaphthalene lactone products 277
- Sommelet–Hauser reaction 310–314

- sperm whale myoglobin 81, 106
- spiro*-lactones 106
- spiro-oxindole products 375
- spirochroman-3,3-oxindoles 348
- spirocyclic cyclopropyl ethers 185
- stereoelectronic biases 231
- $\alpha$ -stereogenic center 111
- stereogenic quaternary carbon center 346
- stereoselective cyclopropanation 28, 29, 36
- stereoselective Doyle–Kirmse reaction 303, 305
- sterically bulky
  - cyclotriphosphazene-containing ester groups 250
- sterically hindered Me<sub>4</sub><sup>t</sup>BuPhos 215, 218
- sterically unhindered pyridine *N*-oxides 204
- Stevens rearrangement 310–312
- strained *trans*-fused dihydrofuranone 205
- strained D-A cyclobutenes 144
- s-trans* metallo-vinyl carbene 146
- s-trans* styrylcarbene 146
- structural studies of carbene
  - intermediates in heme proteins 125–128
- structure-activity relationships (SARs) 325, 362
- styrene 26–30, 32, 35, 38, 39, 97, 100, 101, 104, 106, 119, 122, 124, 125, 127, 128, 178, 179, 183, 372
- styryl diazoacetates 140
- styryl- and related vinyl diazoacetates 160
- styryldiazoacetates 140, 145, 146, 151
- (*Z*)- $\gamma$ -substituent 146
- substituted 3-amino-3-
  - hydroxymethyloxindoles 363
- ortho*-substituted
  - 7-aryl-1,3,5-cycloheptatrienes 177
- ortho*-substituted aryl gold(I) carbenes 190
- substituted benzenes 278
- 7-substituted cycloheptatrienes 174, 180, 195–196
- 7-substituted 1,3,5-cycloheptatrienes 170–171, 179, 187, 193
- ortho*-substituted cycloheptatrienes 191
- 2-substituted/2,6-disubstituted pyridine
  - N*-oxides 204
- $\beta$ -substituted enoldiazoacetates 146
- (*Z*)-4-substituted enoldiazoacetates 158
- 4-substituted enoldiazoacetates 154, 155, 158
- 3-substituted indole derivatives 312, 349
- 4-substituted-1-(methoxymethylene) cyclohexane 150
- ortho*-substituted phenylacetylenes 236
- substituted porphyrins 96
- substituted prolines 341
- (substituted) thiophenols 113
- substituted triarylmethanes 378
- $\beta$ -substituted vinyl diazoacetates 149
- succinimidyl diazoacetates 31, 34
- sulfonamides 213, 328
- sulfone 154, 173, 193, 231, 392
- sulfone-imidazolium gold(I) carbenoids 173
- sulfone-lithium salt 193
- sulfonium ylide 302, 303, 306, 308, 309, 311, 312, 349, 352
- N*-sulfonyl aldimines 328
- sulfoxides as nucleophilic oxidants 201–202
- sulfur ylides 142, 144, 202
- sulfur-containing heterocycles 312
- symmetric allylic selenide 309
- D*<sub>2</sub>-symmetric chiral porphyrins 29
- symmetric diallyl sulfide 303
- symmetric diallylic sulfide 308
- symmetric diaziridines 158
- symmetric thiodiacetates 311
- syn*- and *anti*- $\alpha$ -substituted  $\alpha,\beta$ -diamino acid derivatives 328
- syndiotactic hydroxy-containing poly(alkoxycarbonylmethylene)s 256



- synthetic metal-porphyrin carbene chemistry 99
- synthetic metal-porphyrins 125
- t**
- tandem carbene-cycloaddition reactions 141
- tandem cyclopropanation/Cope rearrangements 140
- L-(+)-tartaric acid 236
- tasimelteon 105–106
- tautomerization process 311
- taxol side chain 358–359
- terminal alkynes 321, 352, 379, 385  
     internal alkynes as the coupling products 386–387  
     multi-substituted allenes 385–386
- terminal diynes 292, 294
- terminal olefins 110, 119, 392
- tertiary aniline substrates 217
- tertiary propargylic alcohols 205, 227
- tethered pyridine *N*-oxide 208
- tethered sulfoxides 201–202
- 1,2,3,4-tetra(acetoxy)naphthalene 288
- tetraarylborate [(NHC)Pd(*nq*)]/borate system 245
- tetrabutylammonium fluoride (TBAF) 155, 289, 358
- tetracyclic dihydroquinoline product 214
- tetrahydrobenz[*b*]azepin-4-ones 215
- tetrahydrofurans 343
- tetrahydropyran 288
- tetrasubstituted allenoates 321–322
- tetrasubstituted carbon stereocenters 339
- thermostable POP protein 124
- thio-Claisen rearrangement 312, 315, 316
- thioalkynes 215, 217
- thiocarbonyl compounds 312
- thioindoles 312
- thiophene 281, 286
- three component polycondensation
- bis(diazocarbonyl) compound, enol-form of 1,3-diketone, and THF 263
- of bis(diazocarbonyl) compound, dicarboxylic acid, and THF 262
- of bis(diazocarbonyl) compound, diol and THF 259–262
- ticagrelor 103, 106–107
- titanium(IV) alkoxides 343
- TMSCF<sub>3</sub> 387
- N*-tosylhydrazones 371, 380, 392  
     palladium-catalyzed cascade cross-coupling reactions 380–382  
     reactions with electrophiles 377–379  
     reactions with nucleophiles 379–380
- transition-metal catalyzed C=C bond formation 264
- transition-metal catalyzed carbene transformation 243–266
- transition-metal-catalyzed C–H bond functionalizations  
     directing-group-assisted C–H bond functionalizations 393–396  
     non-directing-group-assisted C–H functionalizations 391–392
- transition-metal-catalyzed C1 polymerization of diazoacetates
- $\pi$ -allylPdCl-based system-initiated polymerization 246–251
- fluoroalkyl and fluoroaryl group-containing polymers 258–259
- hydroxy group-containing polymers 254–256
- (NHC)Pd(*nq*)/borate-initiated polymerization 245–246
- (*nq*)<sub>2</sub>Pd/borate-and (cod)PdCl(Cl-*nq*)/borate-initiated polymerization 251–254
- oligo(oxyethylene)-containing polymers 256–257
- PdCl<sub>2</sub>-initiated polymerization 244–245
- polycondensation of bis(diazocarbonyl) compounds 259

- transition-metal-catalyzed C1  
 polymerization of diazoacetates (*contd.*)  
   pyrene-containing polymers 257–258  
 transition-metal-catalyzed cross-coupling  
   reactions 371  
 transition-metal-catalyzed X–H bond  
   insertions 67  
 transmetalation 245, 247, 253, 254, 371,  
   374, 381, 388–389, 392  
 tranylcypromine 106  
 tri-substituted 1,2,3-triazoles 387  
 trialkyl-silyl ethynes 386  
 trialkylsilyl substituted terminal alkynes  
   386  
 1,3,5-triazines 336  
 s-triazines 160–161  
 triazole-substituted difluoroalkenes 387  
 tricyclic 2H-pyran-3(6H)-ones 226  
 tricyclic azepines 158  
 triethylamine 244  
 triethylsilane 374  
 trifluoromethyl *N*-tosylhydrazones  
   387–388  
 trifluoromethyl allyl 303  
 $\alpha$ -trifluoromethyl- $\alpha$ -phenyl diazomethane  
   117  
 trifluoromethyl-or  
   phosphonate-containing diazo  
   compounds 373  
 trifluoromethyl-or  
   phosphonate-substituted diazo  
   compounds 373  
 trifluoromethyl-/phosphonate-substituted  
   olefins 373  
 2-trifluoromethylpyridine *N*-oxide 204  
 trifluoromethylthio (SCF<sub>3</sub>) functional  
   group 303  
 trimethyl-substituted cycloheptatrienes  
   180  
 trimethylamine-borane 215  
 trimethylenemethane 157  
 trimethylphosphine gold(I) 177  
 trimethylsilyl cyanide 322  
 (trimethylsilyl)diazomethane  
   (TMSCHN<sub>2</sub>) 372, 376  
 1,3,5-trimethyl-7-styryl-1,3,5-  
   cycloheptatrienes 181–182, 184  
 1,2,5-triol derivatives 346  
 1,2,3-triphenylcyclopropane 174  
 trisubstituted  
   3,6-dihydro-2*H*-1,2-oxazines  
   152  
 trisubstituted tetrahydroquinoxalines  
   328  
 trisubstituted vinyl ethers 149–150  
 tropylium tetrafluoroborate 180  
 TsOH 346  
 two component polycondensation of  
   bis(diazocarbonyl) compound with  
   aromatic diamine 264  
 $\eta^3$ -type anionic ligand 253
- U**
- unprotected pyrroles 339  
 $\alpha,\beta$ -unsaturated 2-acyl imidazoles 346,  
   348  
 $\alpha,\beta$ -unsaturated aldehydes 192  
 $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds  
   185  
 $\alpha,\beta$ -unsaturated carbonyl compounds  
   227, 373  
 unsaturated ketoesters 355  
 $\alpha,\beta$ -unsaturated ketones 227  
 $\alpha,\beta$ -unsaturated  $\delta$ -(*N*-aryl)amino esters  
   345  
 $\beta,\gamma$ -unsaturated *N*-sulfonylimines 362  
 $\beta$ -unsubstituted vinyl diazoacetates 161
- V**
- vinyl azides 145, 150  
 3-vinylbenzofurans 380  
 vinyl boronic acid 373, 382  
 vinyl chromium(0) carbenes 384  
*E*-vinylcyclobutane 390  
*cis*-vinylcyclopropane 179  
 vinyl iodides 376  
 3-vinylindoles 380  
 vinyl Pd-carbene 384  
 vinyl Pd-intermediate 384  
 vinyl polymerization 244

vinyl rhodium(II) carbenes 189  
vinyl substituted  $\alpha$ -diazo pyrazoleamides  
308, 310  
vinyl-Fischer-type carbenes 147  
vinyl-group-containing electrophiles  
381  
vinyl/styryl carbene precursors 184  
vinylazides 149  
vinylcyclopropanes 179, 184, 189, 390  
products 179  
vinylidiazocompounds 140, 142, 152,  
159, 160, 162, 163

**W**

water-assisted diastereoselective proton  
transfer process 312  
water-involved six-membered chair-like  
transition state 312  
well-defined block copolymer 249

whole-cell catalysis 101  
wild-type *Rma* cyt *c* 117  
wild-type P450<sub>BM3</sub> protein 100

**X**

X-H insertion 113–119, 122, 190, 315,  
325

**Y**

ynamide C–C triple bond 221  
ynamides 215, 218, 227, 383, 384  
ynoates 212  
ynones 218, 236

**Z**

zwitterionic intermediates 160  
Aldol-type interception 344  
Mannich-type interception 339  
Michael-type interception 348















