

## Index

### **a**

- acetanilide 343
- acetylenic ketones 572
- acetonitrile 59
- (*-*)-*N*-acetylcolchinol synthesis 446
- (3-acrylamidopropyl)trimethylammonium chloride 633
- acryloyl chloride 633
- N*-acylaldimines
  - enantioselective alkynylation, alkenylation, and arylation 445
- acylate acyliuminium ions 545
- acylhydrazones
  - indium(I)-catalyzed allylboration 419
- N*-acyliuminium ion substrates 427
- acyloxyboranes 26, 99
- acyloxyboronates 25
- addition–deoxygenation process 457
- addition–elimination process 541
  - transpiring through carbocationic intermediate 541
- 1,4-addition reactions, of
  - organotrifluoroborates 535, 536
- 1,2-addition reactions, organoboron compounds 90, 534, 535
- aerobic ketone synthesis 382
- agrochemicals 226
- aldehydes
  - activation 399
  - addition reaction 395–412
  - Brønsted acid catalysis 407–410
  - chiral Brønsted acid catalysis 410–412
  - Lewis acid catalysis 395–403
  - Lewis acid-catalyzed additions with chiral allylboronates 403–407
  - addition reaction of crotylboronates 483
  - aldehyde–amine or interaction between metal and ligand 644
  - aldehyde–boronic acid complex 613

- allylation 393
- competing transition structures in 405
- selective 396
- stereoselectivity 487, 489
- with vivol-*SnCl*<sub>4</sub> catalyst system 411
- allylboration 93, 193, 393
  - chiral catalysis of reactions 394
  - first-generation catalytic system 410
  - selective 397
  - stereoinduction model 488
  - stereoinduction model using chiral  $\alpha$ -substituted allyl neopentyl glycol boronic esters 489
- cyanosilylation 574
- dithiane cleaved using Dess–Martin periodinane 452
- formation of the *trans* lactone 408
- functionality on heteroaryl frameworks 232
- platinum-catalyzed 1,4-diboration of dienal affords 184
- rhodium- and ruthenium catalyzed addition 91
- rhodium-catalyzed oxidative arylation 535
- aldol reactions 26, 97, 297, 560–563
- aliphatic thiol esters 367
- alizarin red S (ARS) 25
- alkane sulfonyl chlorides 365
- alkene boronic acids 365
- alkenes
  - catalytic diboration 177
  - catalytic hydrogenation 514
  - enantioselective diboration 178
  - Heck-type coupling 90
  - hydroxyarylation of 96
  - insertion into Pt–B bond 90
  - metathesis 58, 59
  - platinum-catalyzed diboration 173
  - rhodium- and transition metal-catalyzed additions to 90–92

- silaboration of 191
- *in situ* protective reagent 99
- alk-2-ene sulfonyl chlorides 365
- N*-alkenylation 340
- alkenyl boranes
  - homologation 487
- alkenylboronates 8, 45, 56, 60, 92, 144, 202
  - (*E*)-1-alkenylboronates 57
  - (*Z*)-1-alkenylboronates 60
  - 1-alkenylboronates 144
    - via coupling with B<sub>2</sub>pin<sub>2</sub>/HBpin 144
  - alkenylboronic acids 6, 7, 14, 45, 56
    - addition to β-aryl-β-methyl-α,β-unsaturated pyridylsulfones 290
    - addition to quinolines 454
    - addition to salicylaldehydes 447
    - catalytic enantioselective addition 454
    - chlorination of 85
    - *cis*-alkenylboronic acids 57, 58
    - C–N and C–O cross-coupling 336
    - diastereoselective synthesis of 2-hydroxymorpholines 431
    - formation of enantioenriched 197
    - formation of isoquinoliniumion 446
    - methods for synthesis 46–54
    - oxidation 81
    - preparation by electrophilic trapping, of alkenylmetal intermediates 45
    - protecting group for 19
    - Rh-catalyzed, addition to butenolide 282
    - Rh(I)-catalyzed additions to isocyanates 461
    - substitution patterns 45
    - synthesis 45, 47
    - of alkenylboronic acids (esters) 46
    - transition metal-catalyzed coupling 45, 55
    - transmetalation methods 45
    - *trans*-2-substituted 55
    - used as coupling partner 530
  - (*Z*)-1-alkenylboronic esters 58
  - (*Z*)-1-alkenylboron pinacolates 60
  - alkenyl MIDA boronates 72
  - alkenyl triflates 144
  - α-alkoxyacids 553
  - 4-alkoxy (*E*)-1-alkenylboronates 60
  - 2-alkoxycarbonyl allylic boronate
    - Lewis acid-catalyzed addition 400
  - alkyl aziridines
    - lithiation/borylation 500
  - alkylboronic acids 14, 61, 63, 343, 347, 531
  - alkylboronic esters 61, 63, 66, 68, 71, 99, 485, 531
  - alkylcobaloxime 644
  - N*-alkyldiminoacetate complexes, of boronic acids 25
  - alkyl epoxides
    - for homologation of boronic esters 496
    - lithiated using LTMP 497
    - lithiation/borylation 499
  - alkyl-substituted diarylboronic acids 627
  - 2-alkylthio-1-alkenylboronates 58
  - alkylzirconium reagents 207
  - alkynes
    - catalytic cycle of silaboration 189
    - catalytic silaboration 187
    - *cis*- and *trans*-silaboration of terminal 189
    - diboration 173–176
    - Heck-type coupling 90
    - hydroboration of 55
    - indirect trans-hydroboration 57
    - insertion into Pt–B bonds 135
    - nickel-catalyzed borylative coupling 59
    - Pt-catalyzed diboration reaction of 171
    - rhodium- and iridium-catalyzed trans-hydroboration 58
    - silaborative coupling of 190
    - thermal cis-hydroboration 55–57
    - transition metal-catalyzed *cis*-hydroboration 57, 58
  - 2-(alkynyl)aryl isocyanates 88
  - alkynylboration 203
  - alkynylboronic acids 15, 60, 61
  - alkynylstannane 205
  - alkynyltrifluoroborates 448, 450
    - cross-coupling 530, 531
  - Lewis acid-promoted reaction, with fluoroaziridines 544
  - modified Petasis reaction in conjunction with 543
  - reactions with oxocarbenium ions 542
  - 2-alkysulfanyl oxazolines 370
  - allenes
    - catalytic silaboration 193, 194
    - diboration 177–179
    - intramolecular cyanoboration 203, 204
    - palladium-catalyzed silaboronation of 59
    - transmetalative acylboration 205
  - allylation
    - carbonyl allylation systems based on silicon and tin 393
    - of carbonyl compounds and imine derivatives 93, 393
    - enantioselective allylation of ketimines catalyzed by a chiral diol 421
    - mechanism 414
    - TiCl<sub>4</sub>-promoted allylation of acetals with β-borylallylsilane 201

- allylation reagents
  - classification system for 393, 394
  - *in situ* 420
- allylboration
  - aldehydes 93
  - first-generation catalytic system 410
  - stereoinduction model 488
  - stereoinduction model using chiral  $\alpha$ -substituted allyl neopentyl glycol boronic esters 489
  - stereoinduction model for 483
- allylboronates 63, 93
  - Lewis acid catalysts, screening 396
  - Lewis acid-catalyzed allylboration reaction 395
  - protic acid-catalyzed addition 407
- allylboron compounds 144
- allylic acetates 145
- allylic alcohols 145
  - asymmetric cyclopropanation of 99
- allylic boronates 63, 93, 415
  - $\alpha$ -addition 402
  - additions to
  - aldehydes 93, 395–412
  - imine derivatives 418–422
  - ketones 412–417
  - advantages 395
  - Brønsted acid catalysis 407–409
  - catalytic additions 393–423
  - chiral Brønsted acid catalysis 409–412
  - Lewis acid catalysis 395–402
  - additions with chiral allylboronates 403–407
  - metal-based catalysts, methods 413–417
  - structure 394
  - use 393
- allylic boronic acids 63
- allylic carbonates 96
- allylic halides 145
- allylic phosphates 90
- amidation reactions 540–542
- amide bond formation methods 552
- amide condensation reactions
  - catalysts reactivities comparison 554
  - with catecholborane 555
- amides
  - *N*-arylation 339
  - enantioselective addition to 279
  - homoallylic 421
  - imino 467
  - secondary 461
  - $\alpha,\beta$ -unsaturated Weinreb 286
- amination reactions 540–542
- amino acid adducts of boronic acids 28
- aminoacyl-transfer RNA (tRNA) synthetase 594
- amino alcohols 434
- $\beta$ -amino alcohols
  - preparation 435
  - synthesis from phenyl aziridine 501
- $\alpha$ -aminoalkylboronic acids 71
- aminoborionate catalyst 556
- $\alpha$ -amino boronic esters 467, 468
- 2-amino-3-boronopropionic acid 71
- $\alpha$ -amino esters 431
- 3-aminophenylboronic acid 633, 644, 652
- ortho*-aminophenylboronic acid 28
- 3-aminopyridine 430
- $\beta$ -amino tertiary alcohols synthesis 501
- amphotericin B 255
- AN0128 and AN2690 structures 594
- anionic *N*-heterocyclic carbene (NHC)
  - development 456
  - anti-diastereoselectivity 452
- antihistamine levocetirizine (Xyzal) 446
- anti-homoallylic alcohols 481
- antiplatelet agent 442
- antisense oligonucleotide (ASO) 329
- aprotic solvents 469
- Arachis hypogaea* (peanut) agglutinin lectin (PNA) 610
- arene 41, 42, 150, 365, 372
- 5-arylo-3,4-dihydropyrimidin-2-ones 367
- arylation 456
  - N*-arylation 325, 339, 340
  - of aliphatic amines 341
  - of aromatic amines, and imidazoles 342
  - of benzimidazole to give *p*-tolylbenzimidazole 351
  - electronic effects of phthalimides 349
  - of morpholine, solvent study 350
- ortho*-arylation of aromatic ketones 90
- $\alpha$ -arylation, of carbonyl compounds 95
- aryl benzamide products 465
- arylboronamides 255
- arylboronate probes reaction
  - for hydrogen peroxide 601
- arylboronates 156
  - synthesized using  $B_2pin_2$  140
  - synthesized using  $HBpin$  142
- aryl boronic acid catalyst
  - amide condensation 97, 552
  - *ortho*-halogen substituent, effect 557
- aryl boronic acids 3, 6, 11, 31, 41, 90, 96, 97, 223, 265, 305, 316, 329, 367, 385, 459, 554, 555, 650
  - addition to *in situ* generated imino amides 466

- B–C pi-bonding effect 7
  - C–N cross-coupling with 321–324
  - catalytic copper-mediated 331
  - intramolecular 330
  - C–O cross-coupling
  - intermolecular 316–320
  - intramolecular 320
  - Cu-catalyzed additions, mechanisms for 466
  - deboronation 14
  - heteroarene–heteroarene cross-coupling 330
  - methods for synthesis 32–38
  - preparation by coupling of aryl halides with diboronyl reagents 42, 43
  - preparation by cycloadditions of alkynylboronates 43
  - preparation by direct boronation 43
  - preparation by directed ortho-metallation 40, 41
  - preparation by electrophilic trapping of arylmetal intermediates 31, 32
  - preparation by metal–halogen exchange with aryl halides 32, 40
  - Rh(I)-catalyzed addition with 461
  - Rh(I)-catalyzed enantioselective additions 460
  - rhodium(I)-catalyzed domino reactions 471
  - salicylhydroxamic acid adducts 28
  - sulfonylation of 347
  - transformations of 70
  - transmetalation of aryl silanes
  - and stannanes 41, 42
  - 2-arylboronic acids 96
  - arylboronic esters 39, 40, 88, 90, 139, 338
  - arylboron pinacol esters 77
  - arylboroxines 91, 291, 339, 458, 459
  - aryl bromides 85, 220, 222, 228, 240, 374, 529
  - aryl chlorides 42, 213, 222, 223, 224, 226, 229, 231, 365, 533
  - N-aryl-2-(dialkylphosphino)pyrrole 226
  - 1-arylethlenyl acetates 90
  - arylglycine derivatives, formation 457
  - arylglycine products 463
  - aryl halides
    - azidonation 333
    - borylation 138, 139, 141, 339
    - coupling with diboronyl reagents 42, 43
    - metal–halogen exchange with 32
    - nickel-catalyzed borylations 43
  - aryl methane 365
  - S-aryl-NH<sub>t</sub>-Bu thiosalicylamides 382
  - 2-aryl-4-piperidones 282
  - 6-arylpurine 364
  - aryl silanes
    - transmetalation 41, 42
  - arylstannanes 354
  - aryl sulfamates 253
  - aryl tert-butyl sulfones 364
  - S-aryl thiol esters 367
  - aryltrifluoroborate 452, 514
  - fluorination 541
  - improves the yield and scope of *ortho*-coupling 537
  - nucleophilic ylides generation 520
  - 1-aryl-3-trimethylsilylimidazoles 325
  - aryl triolborates 341
  - ate-complexes
    - 1,2-migration, transition-state structures for 485
  - atom transfer radical polymerization (ATRP) of styrene 633
  - attenuated total reflection IR (ATR-IR) 636
  - Au(I) catalysis 97
  - autoinducers (AI) 592
  - autoxidation 8
  - azaborolidines 27
  - aza-Cope/Lewis acid-promoted Petasis-like reaction 448
  - aza-Cope/Mannich reaction 436
  - azeotropic reflux 552
  - azide-alkyne cycloadditions 70
  - azidoaryltrifluoroborates 522
  - aziridination methodology, applications 564
  - aziridination reaction 561
  - catalytic species, structural elucidation 566
  - of diazoacetates and benzhydryl imines 564
- b**
- bandgap energy 623
  - B-Chiral tetrahedral boronate 6
  - B–C pi-conjugation 6, 7
  - benzaldehydes 90
  - benzene-1,4-diboronic acid 44, 627
  - 1,4-benzenediboronic acid (BDBA) 44, 664
  - 1,3,5-benzenetriboronic acid (BTBA) 660
  - 1,3,5-benzenetris(4-phenylboronic acid) (BTPA) 660
  - benzene–water partition ratio 8
  - benzhydryl imines 561
  - aziridination reaction 564
  - benzoboroxoles 5, 25, 43, 609, 610
    - structure 5, 609
  - benzodiazaboroles 27
    - products 27
  - 1,3,2-benzodioxaborole (catecholborane) 25
  - benzophenone 41, 42, 86, 535

- benzoxaboroles 5
- benzoyl peroxide 43
- benzyl alcohols 496
- benzylamines
  - and aliphatic, aromatic carboxylic acids, condensation reactions 553
  - lithiation/borylation 498
  - salicylaldehydes react with
    - alkenyltrifluoroborates 543
- benzylic alcohols
  - Friedel-Crafts alkylation of 97
  - Ritter reaction 555
- (E)-benzyl oxime ethers
  - borane-mediated reduction 585
- 3,5-(benzyloxy)benzylamine 658
- S-benzyl pyrimidine-4-ones 373
- benzyl thiocyanates 368
- biaryl compounds 241
- biaryl ethers 94, 354
- biaryls 85, 143, 233, 245
  - C–N-linked 331
  - sulfinyl-containing 245
  - synthesis 85
- bidentate phosphorus ligands 270
- bifunctional aminoboronic acids 562
  - catalyst 557
  - utility 560
- bifunctional organoboranes 252–256
- Biginelli reaction 560
  - catalyst for 561
- bimolecular Lewis acid–base
  - complexation 12
- BINOL
  - based bisphosphoramidite 270
  - derivative
    - ketone crotylboration reactions 417
    - derived alkynylboronates 445
    - derived phosphoramidite 460
    - as ligand 400
- bioconjugation 106
- biotinylated arylboronic ester 606
- biotinylated boronic esters 607
- biotinylated F3 polysaccharide 612
- biphenylboronic acid 248, 352
  - side reactions 352
- 4,4'-biphenyldiboronic acid (BPDA) 660
- bipyridines 155
- bis-arylboronate 605
  - structure 606
- bisboronic acid 44, 608
- bisboryl complex 136
- bis(dialkylamino)boranes 203
- 1,2-bis(3,4-dihydroxyphenyl)ethane 640
- bis(diisopropylamino)boron chloride 40
  - 1,1'-bis(diphenylphosphino)ferrocene
    - (dpfp) 534
  - 1,3-bis(diphenylphosphino)propane
    - (dppp) 535
  - bisoxazaborolidinone 584–586
  - 3',6'-bis(pinacolato boron) fluoran 628
  - bis(pinacolato)diboron ( $B_2pin_2$ ) 26, 59, 138, 172, 268, 286, 467
    - 1,1'-bis-substituted ferrocenylaryl ketones 367
  - bis-sulfoxides 276
  - 1,3-bis(*tert*-butoxycarbonyl)-2-methyl-2-thiopseudourea guanidylation reagent 368
  - B3LYP–DFT calculations 399
  - B–N coordination-based macrocycles 655
  - BNC Tagent 28
    - $^{11}B$  NMR experiments 413, 419
  - N-Boc indoline
    - lithiation/borylation 498
  - N-Boc pyrrolidine
    - lithiation/borylation 498
  - N-Boc serine 378
  - BODIPY dyes 373
  - BODIPY functionalization 375
  - $\sigma$ -bonds 171
  - boranes
    - homologation 492–496
    - secondary lithiated carbamates
    - enantiodivergent reaction 492–496
  - borate complex 560, 561
  - borate derivatives
    - as catalysts 551
    - chiral boron-based catalysis
    - bisoxazaborolidinone 584–586
    - cationic oxazaborolidine catalysts 567–576
    - oxazaborolidinone catalysts 577–581
    - spiroborate catalysts 581–584
    - tartaric acid-derived boronate ester 586
    - VAPOL/VANOL+ $B(OPh)_3$  catalysts 561–567
    - nonchiral boron-based catalysis 551–561
    - aldol and Biginelli reactions 560, 561
    - amide condensation 551–558
    - esterification reactions 559, 560
  - boric acid
    - Al-2 complex 592
    - amide condensation catalyst 558
    - catalyzed by  $\alpha$ -hydroxycarboxylic acids 560
  - boronate anion 9
  - boronate-based hydrogen peroxide
    - probes 599
  - boronate-based materials 108, 623
  - boronate-based networks 658

- boronate diesters 646  
boronate esters 39, 72, 106, 266, 268, 586  
– in Rh-catalyzed enantioselective conjugate additions 266, 268  
– structures 595  
boronate formation  
– Fc-fused dectin-1 612  
boronate-linked materials 108, 625  
boronate materials 108, 631  
boronate reagents, advantages 431  
boron hypercoordination 6  
boronic acid-based compounds  
– applications 605  
boronic acid/boronate-based probes  
– design principle 597  
boronic acid derivatives 2  
– acididc character 9  
– applications  
– as antimicrobial agents and enzyme inhibitors 103–105  
– in bioconjugation and labeling 106, 107  
– in chemical biology 107, 108  
– in materials science and self-assembly 108, 109  
– in neutron capture therapy for cancer 105  
– as protecting groups 99, 100  
– as reaction promoters and catalysts 97–99  
– as supports for immobilization 100–102  
– in transmembrane transport 105, 106  
– use as receptors and sensors 102, 103  
– as catalysts 97, 551  
– chemical stability 12  
– chiral boron-based catalysis  
– bisoxazaborolidinone 584–586  
– cationic oxazaborolidine catalysts 567–576  
– oxazaborolidinone catalysts 577–581  
– spiroborate catalysts 581–584  
– tartaric acid-derived boronate ester 586  
– VAPOL/VANOL+B(OPh)<sub>3</sub> catalysts 561–567  
– C–N and C–O cross-coupling 338–342  
– boronic esters 338–342  
– boroxines 338–342  
– trifluoroborate salts 338–342  
– general types and nomenclature 2  
– nonchiral boron-based catalysis 551–561  
– aldol and Biginelli reactions 560, 561  
– amide condensation 551–558  
– esterification reactions 559, 560  
– safety considerations 9  
– structure 612  
– and properties of 2  
boronic acid–diol binding mechanism 612  
boronic acid-end-functionalized polymer 633  
boronic acid-functionalized polymer 634  
boronic acids  
– AI-2-mediated quorum sensing inhibition  
– IC<sub>50</sub> values 593  
– applications  
– in affinity purification 100  
– in boron neutron capture therapy 105  
– in catalysis 97  
– in chemical biology and medicinal chemistry 103, 107, 591–593  
– as protecting groups 99  
– in transmembrane transport 105  
– carbohydrate biomarker binding agents  
– and sensors 102, 607–617  
– as potential medicinal agents 591–596  
– antimicrobial and antifungal agents 593–595  
– bacterial quorum sensing inhibitors 592–593  
– bortezomib, story 595–596  
– reactive oxygen species detection, probes for 597–603  
– *in vivo* carbohydrate imaging  
– MRI and PET agents 603–607  
boronic anhydrides 15, 621  
boronic esterification 639  
boronic esters 1, 3, 16, 624  
– allylboron reagents  
– synthesis and application 487–492  
– asymmetric homologation 479–502  
– iterative 481  
– Matteson-type substrate controlled 480  
– reagent controlled 480  
– bimolecular Lewis acid–base complexes with 13  
– boranes/boronic esters, direct homologation 482–487  
– boranes/boronic esters homologation, lithiated secondary carbamates for 492–496  
– boronic acid–diol (sugar) equilibrium 23–25  
– boronic esters homologation, lithiated epoxides for 496–500  
–  $\alpha$ -carbamoyloxy-alkylboronates  
– synthesis and reaction 481, 482  
– cleavage 19–23  
– pinanediol boronic esters 21  
– diol-catalyzed additions  
– to unsaturated carbonyl compounds and acetals 92  
– equilibrium formation from diols 23  
– homologation 486, 493–495

- lithiated aziridines for 500, 501
- hydrolysis 19–23
- two-phase system 22
- multiple stereocontrolled homologations 486
- other C–C bond forming reactions 93
- reversible hydrolysis 22
- secondary lithiated carbamates, enantiodivergent reaction 496
- self-assembled, reversible tetraboronic ester cages 24
- stoichiometric formation, in nonaqueous conditions 16–19
- transesterification 22
- trialkylboranes homologation
- benzyllic *N*-linked lithiated carbamates 492–496
- boronic-modified thymidine triphosphates
- structures 615
- boron–lead transmetalation 95
- boron neutron capture therapy (BNCT) 105, 605
- boron–nitrogen heterocycles 27
- 3-boronoacrolein 3
- borono-hydrazone 626
- 4-borono-phenylalanine 42
- p*-boronophenylalanine 615
- 4-boronophenylalanine, structure 616
- 2-boronyl-allylsilanes 59
- boronyl group 3, 6, 10, 14, 19, 70, 72, 103
- borosilicate cyclic compounds 642
- boroxinate 565
- boroxines 1, 15, 266, 565, 621
- cyclic anhydrides 15, 16
- linkages 659
- networks synthesized via ATRP 666
- with the Rh/phosphoramidite 282
- bortezomib (*Velcade*<sup>®</sup>) drug 467, 595
- carinolamide metabolites 596
- effect 595
- structures 596
- synthesis 469
- $\beta$ -borylallylsilanes 194, 200, 201, 202
- borylation
- alkanyl halides 143
- allylic acetates 145–148
- allylic alcohols 145–148
- allylic halides 145–148
- aryl halides 42
- benzyllic halides 148
- bis(boryl) 155
- cyclopentadienyl ring of ferrocene 155
- halides, via coupling of H–B and B–B compounds 137–143
- iodoarenes 142
- metal-catalyzed, H–B and B–B reagents 137
- naphthalene 155
- *ortho*-selective
- arenes directed by SiMe<sub>2</sub>H 158
- benzoates 159
- perylene derivatives 155
- porphyrins 156
- pyrene derivatives 155
- regioselectivity in aliphatic 161
- rhodium-catalyzed 150
- silicon-tethered diene 87, dehydrogenative 192
- tetra(boryl) derivatives 155
- triflates, via coupling of H–B and B–B compounds 137–143
- via C–H activation 148
- aliphatic C–H bonds 148–151
- alkanyl C–H bonds 151–153
- aromatic C–H bonds 153–159
- vinylcyclopropanes 145
- meta*-borylation 43
- ortho*-borylation 43
- 5-borylpyridine 155
- 4-borylpyridines 155
- 2-boryl-3-silyl-1-alkenes 194
- boryl-transition metal complexes 136
- 4,5-bridged 1,2,5-triazepine-3,6-diones synthesis 439
- ortho*-bromobenzeneboronic esters 96
- bromo-boronolactonization 97
- (6-bromopyridin-3-yl)boronic acid reaction 434
- 2-bromo 5-pyridylboronic acids 4
- Brønsted acid-activated catalysts 573
- Brønsted acid-assisted Lewis acid (BLA) 567–572, 575
- Brønsted acid catalysis 407–409, 565
- further advances 410–412
- mechanistic studies 410
- protic acid catalyzed allylboration, discovery 407–408
- reversal of diastereoselectivity 409
- Brønsted acidity 12
- Brønsted acids 407, 408, 422
- Brønsted base 9
- Brown's amineborane 584
- Br-substituted derivatives of BINOL 416
- Brunauer–Emmett–Teller (BET) surface area 660
- Buchwald–Hartwig coupling reaction 315
- N*-Bus-protected phenyl aziridine 500

- 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ( $\text{BmimBF}_4$ ) 348  
 1-*n*-butyl-3-methylimidazolium triflate ( $\text{BmimOTf}$ ) 348  
*N*-butylpyrrolidinone (NBP) 553  
*N*-*tert*-butylsulfinylaldimines.  
 – copper(I)-catalyzed boration of 468
- c**
- cages. *See* macrocycles  
 capsules  
 – built by boronic ester formation 640  
 – constructed from cavitand tetraboronic acid and 640  
 carbamates 253  
 $\alpha$ -carbamoyloxyalkylboronates 481  
 – synthesis and reaction 482  
 $\alpha$ -carbamoyloxy-crotylboronate 481  
 carboboration 202, 203  
 – transmetalative 205  
 carbohydrate binding agents (CBAs) 595  
 carbohydrate biomarker binding agents/  
 sensors 102, 607–617  
 – boronic acids, application 617  
 – cell surface carbohydrate binders 608–613  
 – challenging issue 608  
 – genetically encoded boron-containing amino acid 108, 615–616  
 – glycoproteins aptamers for 613, 614  
 – tetraserine motif, cell permeable sensors 106, 616  
 carbon–boron bond 522  
 carbon–carbon bond  
 – Cu(I)-catalyzed desulfitative 385  
 – forming processes 85  
 -- transition metal-catalyzed cross-coupling 85  
 – forming reactions  
 -- with activated electrophiles 542–546  
 – forming transformation 546  
 carbon–heteroatom bond forming processes 94  
 – copper-catalyzed coupling 94  
 carbonyl allylboration 93, 393  
*ortho*-carboxamido phenylboronic acids 40  
 carboxylate anion 367  
 carboxylate ligand 380  
 carboxylic acids 74  
 4-carboxy-2-nitrophenylboronic acid 4  
*p*-carboxyphenylboronic acid 14  
 catalyst–dienophile complex 571  
 catalyst system 422, 555  
 catalyst turnover number (TON) 226, 228
- catalytic copper turnover, under anaerobic conditions 384  
 catalytic cycle 159–161  
 – for allene silaboration 196  
 – anaerobic Cu-catalyzed desulfitative catalysis 387  
 – for aromatic C–H borylation 160  
 – proposed for Cu-catalyzed methoxylation of tolylboronic ester 354  
 catalytic enantioselective Petasis borono-Mannich reaction  
 – biaryl phenol catalyst 432  
 catalytic enantioselective synthesis  
 – chiral  $\alpha$ -substituted allylic boronates 406  
 catalytic hydrogenation reactions 514, 515  
 catalytic systems 400  
 catalytic transmetalative alkynylboration 206  
 catechol esters 6, 12  
 catechol-functionalized polystyrene resin 76  
 cationic 4-borono-*N*-methylpyridinium iodide 553  
 cationic oxazaborolidine catalysis 568  
 cationic oxazaborolidinium catalysts 28  
 cationic palladium catalyst 465  
 cationic palladium complex 463  
 cationic palladium(II) catalysts 464  
 cationic Pd-catalyzed arylation, mechanism 463  
 C–C bond forming processes 2  
 CDP840 378  
 cedranediolborane 42  
 cell culture test 604  
 $3,3'-(\text{CF}_3)_2\text{-BINOL}$  allylboronate 413  
 C-glucals 153  
 C-glycosylation 90  
 C–H activation 43, 536, 537  
 Chan–Lam coupling reaction 94, 315, 316  
 – additional N-containing substrates 332–335  
 – application in solid-phase synthesis 324  
 – substrate selectivity and reactivity 335, 336  
 – use of alkylboronic acids 343  
 chemical exchange saturation transfer (CEST)  
 – imagining sequence 605  
 chemoselective transformations  
 – compatible with boronic acid derivatives 70  
 – compounds containing a boronic acid (ester) substituent 63, 64  
 --  $\alpha$ -boronyl-substituted carbanions and radicals 66–68  
 -- oxidative methods 64  
 -- reactions of  $\alpha$ -haloalkylboronic esters 68, 69  
 -- reductive methods 64, 65

- C–heteroatom cross-coupling  
 – methodology 356  
 chiral acyloxyboranes 99  
 chiral allylboronates  
 –  $\text{Sc}(\text{OTf})_3$ -catalyzed enantioselective addition 404  
 – uses 403  
 chiral aziridine-2-carboxylate ester 563  
 chiral bis-Lewis acid  
 – catalytic, and computational studies 585  
 – design 586  
 chiral bis-sulfoxide ligands  
 – for Rh-cat enantioselective conjugate addition 276, 277  
 chiral boron-based catalysis  
 – bisoxazaborolidinone 584–586  
 – cationic oxazaborolidine catalysts 567–576  
 – oxazaborolidinone catalysts 577–581  
 – spiroborole catalysts 581–584  
 – tartaric acid-derived boronate ester 586  
 – VAPOL/VANOL+ $\text{B}(\text{OPh})_3$  catalysts 561–567  
 chiral Brønsted acid catalysis 409–412  
 – development and mechanistic studies 410–412  
 – discovery, and optimization 410  
 chiral cationic rhodium complexes 269  
 chiral diol-catalyzed ketone allylboration reactions  
 – transition states in 417  
 chiral 3,3'-disubstituted-2,2'-binaphthol (BINOL) molecules 444  
 chiral ligands  
 – as active rhodium precatalysts 269  
 – atroposelective Suzuki–Miyaura cross-couplings using 242, 244  
 – axial chirality induced by 241  
 – bearing a phosphorus center 276  
 – in catalytic asymmetric reactions 332  
 – for enantioselective arylation of imines 458  
 – use on Lewis acid in catalytic allylboration reaction 400  
 chiral oxazaborolidines 28  
 chiral  $\beta$ -substituted aldehydes 448  
 chiral vaulted biaryl phenol catalysts 431  
 chloramine-T 541  
 chloroalkanols 97  
 chloroboranes 28, 30, 81, 205, 540  
*m*-chloroperbenzoic acid 512  
 4-chlorophenylboronic acid 385  
 2-chloropyridine 155, 229  
 2-chloro 5-pyridylboronic acids 4  
*meta*-chlorosulfonyl arylboronic acids 72  
 C–H–O hydrogen bonding 647  
 cinnamaldehyde  
 – Diels–Alder reaction 586  
 circular dichroism (CD) 645  
*cis*-alkenylboronic acids 58  
*cis*-1,2-diboronylalkenes 59  
 (*S*)-clopidogrel (Plavix<sup>®</sup>) 442  
 (+/−)-clopidogrel synthesis  
 – Petasis borono-Mannich reaction 443  
 $^{13}\text{C}$  NMR alpha effect of boronate group 6  
 cobaloximes 644  
 – serve as Lewis basic moieties 644  
 cod containing rhodium precursor 269  
 COF 108, 662  
 – based on boronate linkages 660  
 – based on boronate linkages arose from 660  
 – based on phthalocyanine tetra (acetone) 667  
 – COF-5, first reported 660  
 – COF materials 108, 659  
 – crystalline porous solid COF-1 108  
 – 3D COFs based on triangular and tetrahedral units 666  
 – 2D COFs with boroxine ring 664  
 – first photoconductive COF 665  
 – incorporating alkyl chains 663  
 – with luminescent, and semiconducting properties 664  
 – for multilayer LED devices 667  
 – PPY-COF 664  
 combinatorial transition metal catalysis 273  
 complex hybrid structures 655–658  
 compounds, based on boroxine rings 657  
 condensation catalysts 552  
 controlled pore glass (CPG) 609  
 coordinative interactions 622, 624  
 – boronate polymers incorporate 630  
 copper-based couplings 455  
 copper–boron transmetalation 58  
 copper catalyst 71, 344  
 copper-catalyzed coupling 94  
 copper-catalyzed oxidative addition 465–467  
 copper-catalyzed stereospecific couplings 90  
 copper-catalyzed variants 43  
 copper(I)-centered compounds  
 – coordinated by four boronic acids 648  
 copper(I) 3-methylsalicylate ( $\text{CuMeSal}$ ) 368  
 copper(I) thiophene-2-carboxylate (CuTC) 368, 375  
 copper-mediated C–C coupling reactions 357  
 copper-promoted coupling process 522  
 Corey–Bakshi–Shibata (CBS) reduction  
 – for carbonyl and imine reductions 587  
 – of prochiral ketones 567  
 Corey–Fuchs reaction 438

- coumarin-based probe 601  
 coupling reaction of B–B or B–H compounds 135  
 covalent bonding 622, 624  
 covalent bonding boronate assemblies 637–653, 659–667  
 covalently bonded boronate assemblies 624–628  
 covalent organic frameworks 108, 624  
 cross-coupling reactions 85, 526–534  
 – Heck transformations 60, 90, 526  
 – of potassium aryl/  
     heteroaryltrifluoroborates 527, 528  
 – Suzuki–Miyaura transformations 85, 526  
 cross-coupling reagents 30  
 cross-metathesis 58, 70  
 crotylboronates 397, 401, 404, 415, 420,  
     481, 483  
 – synthesis and aldehyde addition reaction 483  
*E*-crotyl pinacolboronate  
 – Sc(OTf)<sub>3</sub>-catalyzed addition 398  
 C–S and C–Se/C–Te cross-coupling 346–348  
 C–S cross-coupling chemistry 347  
 C<sub>2</sub>-symmetric cationic *N*-heterocyclic carbene Pd(II) diaquo complex 464  
 CuBr/*t*-BuOOH system 466  
 Cu-catalyzed aerobic coupling 382  
 Cu-catalyzed cross-couplings  
 – under anaerobic conditions 385  
 Cu-catalyzed desulfitative coupling  
 – under anaerobic conditions 386  
 Cu-catalyzed methoxylation, of tolylboronic ester 353  
 Cu-catalyzed N/O-arylation 352  
 Cu-catalyzed oxidative N/O-arylation reactions 349  
 Cu-catalyzed thiol ester/boronic acid cross-coupling 384  
 CuF-catalyzed ketimine allylboration reaction  
 – catalytic cycle 421  
 CuF–DuPHOS system 419  
 Cu<sup>I</sup> carboxylate 380  
 Cu(I) carboxylate cofactor 368  
 Cu<sup>I</sup>-dioxygen reactions 384  
 Cu<sup>I</sup> diphenylphosphinate 367, 380  
 Cu(I)-phenanthroline metal–ligand interactions 646  
 Cu(I) thiolate 385  
 Cu-mediated desulfitative couplings 379  
 CuTC cofactor 371  
 Cu-templated coupling reaction 384  
 cyanobenzoic acids 553  
 cyanoboration 203, 204  
     – alkynes 203, 204  
     – allenes 204  
 cyanoboration, of homopropargylic alkynes 59  
 cyclic α,β-unsaturated esters 279  
 cyclic *N*-acyliminium ions.  
 – diastereoselective control 451  
 cyclic (alkyl)(amino) carbenes (CAAC) 230  
 cyclic aryl triolborates 268, 341  
 cyclic boronic esters 637  
 cyclic dialkoxyboranes 25  
 cyclic esters 621  
 – formation 612  
 cyclic organoboroxine 266  
 cyclic thioamides  
 – C–C vs. C–S cross-coupling with boronic acids 371  
 cyclic trialkoxyborate salts 31  
 cycloadditions 26  
 – of alkynylboronates 43, 60  
 – followed by aromatization 32  
 – applications 573  
 – azide-alkyne 70  
 – of dibutylethylene boronate 7  
 – generation of silylene-palladium species 188  
 – Huisgen dipolar cycloadditions 520  
 – product of cyclopentadiene and acrolein 568  
 cycloalkenyl halides 143  
 cyclobutanones 90  
 cyclobutenediones 373  
 cyclodimerization, of D-glucosamine 97  
 1,3-cyclohexadienes 193  
 2-cyclohexenone 269  
 cyclohexylboronic acid 382  
 cyclopropanation 71  
*N*-cyclopropanation reaction 344  
 – with cyclopropylboronic acid 343  
 – of indoles 343  
 – of NH-containing azoles, amides, and sulfonamides 344  
 cyclopropylamides 343  
*N*-cyclopropylation 344  
 cyclopropylboronates 72  
 cyclotriicatechylene 639  
 cytosolic fluorescence 598  
 cytoxazole enantiomers synthesis 440
- d**
- deaminoborylation, of aniline 43  
 Dean–Stark apparatus 25  
 decarbonylation vs. transmetalation 376  
 (–)-decaestrichtine D synthesis 491

- one-pot three-component coupling reaction 492
- $\pi$ -deficient heteroaromatic thioethers 368
- dehydrogenative coupling
  - for preparation of alkenylboron compounds 151
- dendrimer 658
- density functional theory (DFT) method 443
- D-erythro sphingosine 377, 378
- Dess–Martin oxidations 513
- Dess–Martin periodinane 452
- desulfitative couplings 88, 368–370
  - Cu-mediated 379, 386
  - first-generation 381
  - second-generation 381
- desulfitative functionalization 372
- desulfitative thiol ester–boronic acid cross-couplings
- under aerobic conditions catalyzed by Cu only 381, 382
- D-fructose 24, 97, 105, 631, 633, 634
- DFT calculations 179, 292, 399, 417, 586
  - for bonding 6
- D-galactose 44
- D-glucose 24, 97, 278, 648
- diacylboronate 557
- diacyloxyboronates 25
- dialkoxyanthracene (DAA) 613
- dialkoxyboranes 25, 26, 43
- dialkoynaphthalene (DAN) 613
- ortho*-dialkylaminomethyl group 11
- N,N*-dialkylated benzylamines 40
  - *ortho*-lithiation 40
- diamines, as protecting groups 99
- 1,8-diaminonaphthalene 256
- 1,8-diaminonaphthalene adducts 28
- diaryl disulfides
  - aryl- or alkylation of 387
- diaryl-1*H*-indenol formation 469
- diastereoisomer 246, 272, 273, 282, 293
- diastereomeric 1,3,5-triols 203
- diastereoselectivity 100
  - Lewis acid-catalyzed allylboration/lactonization 403
- Rh-catalyzed conjugate addition 282, 283
  - synthesis of axially chiral arylsuccinimides 285
- diazaborinanes 3
- diazaboroles 28, 626
- diazaborolidines 3
- diazoacetates
  - aziridination reaction 564
- diazocyclopentadiene 96
- diazoesters 90
- diazomethanes 183
- dibora species 524
- diboration 59, 172
  - alkenes 176–183
  - alkylidene carbenoids 183
  - alkynes 59, 173, 175, 176
  - allenes 176–183
  - catalytic
    - conjugate, of  $\alpha,\beta$ -unsaturated carbonyl compounds 181
    - of diazomethanes 183
    - of imines 182
  - coupling of 1,3-dienes, with aldehydes 180
  - 1,2-diboration of 1,3-pentadiene 179
  - 1,3-dienes 176–183
  - dimerization of isoprene 180
  - enantioselective diboration of 1,3-dienes 180
  - methylenecyclopropanes 176–183
  - products, synthetic applications 183–185
  - reaction mechanism 176
  - reagents 172, 173
  - selected examples 174, 175
  - stoichiometric reaction 176
- diborane receptors 12
- diboronic acid 44, 107, 138, 145, 625, 626, 637, 669
- diboronylation
  - and silaboration of unsaturated compounds 46
  - of unsaturated compounds 59
- diboronyl esters 26, 42, 43
- diboronyl reagents 26
- diborylation 59, 63, 135, 155
  - 1,4-diboryl-2-butene 184
  - 2,4-diboryl-1-butene 185
  - 1,2-diborylhexane 184
  - 1,2-diboryl-1-hexene 34, 183
  - 2,3-diboryl-1-propene 184
- 1,3-dicarbonyl compounds 94
- DICHEDE esters 21, 22
- $\alpha,\alpha$ -dichloroaldimines
  - boron-based 543
- dichloroboranes 28, 30
  - 1,2-dichloroethane (DCE) 430
- dichloromethane solvent 513
- Diels–Alder adduct 566, 571
- Diels–Alder reactions 97, 525, 526, 571, 574, 578, 581
  - of acetylenic ketones 572
  - 1- and 2-substituted cyclopentadienes 570
  - broad spectrum 567
  - catalyst system 573

- catalyzed by Lewis acid-assisted Lewis acid 569
  - chiral Lewis acids effectively catalyze 567
  - LLA catalyst for 569
  - provide cycloadducts with dienes 7
  - using  $\text{SnCl}_4$  568
  - diene ligands 274, 276
  - diethanolamine 22, 72, 96
  - diethanolamine boronates 27
  - N,N*-diethanolaminomethyl polystyrene 75, 76
  - N,N*-diethyl *O*-carbamates 41
  - diethylzinc 96
  - 3,5-diformylphenylboronic acid 658
  - dihaloboranes 29
  - 2,4-di(het)aryl-pyrido[3,2-d]pyrimidines 373, 374
  - 9,9-dihexylfluorene-2,7-diboronic acid 627
  - dihydroalkylboranes 29
  - 1,2-dihydroisoquinoline products 446
  - 1,2-dihydroquinolines 448
  - dihydroxylations 100
  - (*S*)-4,5-dihydroxypentane-2,3-dione 592
  - 2,3-dihydroxypyridine 658
  - 3,4-dihydroxypyridine 658
  - (diisopropylamino)borane 142
  - 2,6-diisopropylphenol 577
  - 4,4'-dimethylbiphenyl 351
  - dimethylphenylsilylpinacolatoboron 268
  - (*R,R*)-(+)1,2-di(1-naphthyl)-1,2-ethanediol 410
  - dinuclear supramolecular macrocycles 646
  - diol–allylboronate complex 417
  - diol-based polyfluoroalkyl linkers 76
  - diol–boronic acid complexation 25
  - diol–Lewis acid complex 411
  - diols
    - boronic acid supports for 101
    - protecting groups 99
  - (*E*)-anti-1,4-diols synthesis 492
  - dioxaborinanes 3
  - dioxaborolanes 3
  - diphosphine ligand (DuPHOS) 264, 270, 284, 301, 413
  - diphosphines 217
  - 2,2'-dipyridinedicarboxylic acid (DPDCA) 155
  - $\beta,\beta$ -disubstituted  $\alpha,\beta$ -unsaturated ketones 268
  - 2,2-disubstituted-1-alkenylboranes 60
  - N,N'*-disubstituted imidazolylidines 217
  - 3,5-di-t-butylphenol 335
  - 1,3,2-dithiaborolane 26
  - diversity-oriented synthesis (DOS)
    - concept 434
  - (+)-dodoneine synthesis 412
  - domino aza-Cope/Petasis-like reaction 450
  - Dötz cycloaddition 43
    - Fisher chromium carbene complexes 43
  - double-allylation reagents 406
  - DPD–boric acid complex 592
  - DPD (*S*)-4,5-dihydroxypentane-2,3-dione 593
  - drugs
    - antifungal 104, 593
    - boronic acid-based enzyme inhibitors 104
    - feedback-controlled delivery systems for 591
  - dynamic light scattering (DLS) 612
- e**
- Egg PC-X 612
  - electron-deficient alkenes 461
  - electron-deficient amines. *See* 3-aminopyridine
  - electronic effects 160
  - electrophiles
    - metal–halogen exchange reactions with 523
  - electrospray mass spectrometry 557
  - enantioselection 266, 413
    - BINOL-based reactions 428
    - conjugate addition
      - generalized model 267
      - stereocontrol model 267
    - conjugate borylation
      - of  $\alpha,\beta$ -unsaturated carbonyl compounds 182
    - diboration of 1,3-dienes 180
    - (*E*)-anti-2-ene-1,4-diols synthesis 491
  - enones
    - 1,4-addition to 137
    - arylations of 460
    - asymmetric Mukaiyama–Michael reaction 577
    - $\beta$ -substituted 264
    - Diels–Alder reaction of acyclic enones 580
    - enantioselective conjugate addition to 278
    - nickel-catalyzed borylative coupling 59
    - nucleophilic addition to 92
    - Pd-catalyzed addition to 300
  - epoxidation
    - of alkenylboronic esters 64
    - of 1-alkenyltrifluoroborate salts 31
    - synthesis of (*E*)-anti-2-ene-1,4-diols 491
  - esterification reactions 559, 560
    - mechanistic pathway for 560
  - ester-linked polymers 626

- 1,2-ethane dianion 525  
 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) 453  
 ethyl aquacobaloxime 644  
 ethylbenzene 150  
 ethyl benzoate 41  
 ethylboronic acid 1, 99  
 ethyl diazoacetate (EDA) 561  
 ethylene dichloride 74  
 5-ethyl-2-methylpyridine-borane (PEMB) 516  
 – chemical reactivity 516  
 5-exo-dig cyclization 471  
*E/Z* selectivity 60
- f**  
 factor Xa inhibitors 326  
 (+)-faranal synthesis 486  
 – one-pot quadruple homologation sequence 487  
 Ferrier rearrangement mechanism 542  
 ferrocene-derived bifunctional aminoboronic acid catalysts 557  
 field effect transistor (FET) 608  
 $[^{18}\text{F}]$ -labeled aryltrifluoroborate anion 606  
 Florio's procedure 497  
 fluorescent bisboronic acid compound 616  
 fluorescent boronic acid-containing DNA aptamers 614  
 fluorescent catechol derivatives 25  
 6-fluoropurine, 6-(3-methylbutyl)sulfanylpurine 364  
 2-formylboronic acid 29  
 formyl-substituted organotrifluoroborates reaction  
 – Horner–Wadsworth–Emmons reaction 519  
 – with nonstabilized ylides 518  
 – with stabilized ylides 518  
 Föster resonance energy transfer (FRET) 598  
 FRET-based hydrogen peroxide reagent 600  
 Friedel–Crafts alkylation  
 – of benzylic alcohols 97  
 fucosylated antigens 608  
 fumarate 284  
 F-Vivol-SnCl<sub>4</sub>-catalyzed *E*-crotylboration 412
- g**  
 Gd-based MRI contrast agents 603  
 gelation tests 625  
 $\alpha$ -*gem*-difluoro ketones 529  
 genetically encoded boron-containing amino acid 615–616  
 glucuronamide-based disaccharides 625
- glycoproteins  
 – aptamers for 613, 614  
 – terminal glycosylation state, visual detection 610  
 glyoxylate-derived *N*-*tert*-butylsulfinylimine 463  
 gold-catalyzed oxidative couplings 90  
 grand canonical Monte Carlo (GCMC) simulations 659  
 Grignard reagents 39, 264, 364  
 Grubbs' catalyst 441, 442, 453  
 Grubbs first-generation catalyst 65, 441  
 Grubbs' ring-closure metathesis reaction 336
- h**  
 $\alpha$ -haloalkylboronic esters 68, 69  
 haloarenes 139, 141, 142  
 – borylation of 42, 137  
 – coupling at sterically hindered *ortho*-positions 42, 143  
 – homocoupling products 138  
 – using PdCl<sub>2</sub>(dpff) and KOAc in DMSO 144  
 haloboronamide 254  
 halodeboronation  
 – alkarylboronic acids and esters 83–85  
 – arylboronic acids and esters 81–83  
 halogenation  
 – employing pinacol arylboronates 81  
 – with halosuccinimides 70  
 – reaction with CuBr<sub>2</sub> 81, 471  
 – and subsequent coupling using Pd(0) 537  
 – for various types of alkarylboronic acids 84  
 halomethyltrifluoroborates reaction 511  
 4-halo-*n*-butyl thiol esters 366  
 halosuccinimides 70  
 Hammett value 651  
 Hantzsch–Widman system 3  
 H-bonding 3, 622  
 heats of reaction 13  
 Heck couplings 60, 143  
 Heck-type reactions, with boronic acids 90  
 hemi-heterocyclic boronic ester derivatives 29  
 hepatocellular carcinoma (HCC) 608  
 heteroarene organotin 365  
 heteroaromatic rings, functionalization of 372, 373  
 heteroaromatic thioethers 368  
 $N$ -heteroaromatic thioethers 371  
 heteroarylboronates 44, 157  
 heterocombination of ligands 274  
 $N$ -heterocycles 344  
 heterocyclic aromatic boronic acids 44  
 heterocyclic boranes 25, 26

- N-heterocyclic carbene (NHC) 216, 219, 270, 278  
 heterocyclic derivatives, of boronic acids 27  
 heterocyclic frameworks synthesis  
 – sequential Petasis borono-Mannich aza-Cope/Mannich route 437  
 heterocyclic thioamide fragments  
 – coupling with boronic acids 370  
 hetero Diels–Alder reaction 565, 567  
 hexafluoroisopropanol (HFIP) 543  
 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) 431  
 hexafluorophosphate (HBTU) reagent 437  
 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) 660  
 Hiyama coupling conditions 200  
 Hodgson protocol 496  
 (*E*)-anti-homoallylic alcohols 489  
 (*E*)-syn-homoallylic alcohols 488  
 (*Z*)-anti-homoallylic alcohols synthesis 487  
 homocombinations of ligands 274  
 homologation process 483, 489  
 – of boranes and boronic esters 485  
 Hoppe's lithiated carbamates  
 – applications 479  
 Hoppe's procedure 481  
 Horner-Wadsworth-Emmons reactions 517–520  
 Huisgen dipolar cycloaddition reaction  
 – Sharpless/Meldal “Click” modification 520  
 Huisgen dipolar cycloadditions 520–522  
 hydrazines 29, 332, 436, 437  
 $\beta$ -hydride elimination 533  
 hydroboration reactions 55, 524, 525  
 hydrocinnamaldehyde 398  
 – methallylboration, Vivol vs. F-Vivol 411  
 hydrogen peroxide  
 – arylboronate probes reaction 601  
 – boronate-based hydrogen peroxide probes 599  
 – FRET-based hydrogen peroxide reagent 600  
 hydrolysis reactions 538, 539  
 hydrosilylation 171, 185, 191  
 $\alpha$ -hydroxyacids 103, 553  
 $\beta$ -hydroxy allylsilanes 489, 491  
 (*Z*)-anti- $\beta$ -hydroxy allylsilanes synthesis 491  
 $\alpha$ -hydroxybenzenecarbonyl systems 653  
 $\alpha$ -hydroxycarboxylic acids 103  
 – boric acid catalyzed by 560  
 – chemoselective esterification 559  
 – esterification 559  
 4-hydroxymethylbenzoic acid (HMBA) resin 436  
 5-hydroxypiperidin-2-ones 450  
 4-hydroxypyrrolidin-2-ones 450  
 hydroxyrhodium 264
- i*  
 imine allylation reaction 93, 418  
 imine derivatives additions 93, 418–422  
 – diol-based catalysts 421, 422  
 – metal-based catalysts 419–421  
 imines 93, 182  
 iminium ion 430  
 iminiums 93  
 iminocyclitol 433  
 – formation 434  
 immunosuppressive agent, FTY720 438  
 – synthesis 440  
 indole substrates  
 – Petasis-like reaction 449  
 indolylboronic acid 44  
 $\pi$ – $\pi$  interactions 639  
 intermolecular alkylation 366  
 intermolecular transmetalative carboboration 207  
 internal charge transfer (ICT) 602  
 intramolecular  $\beta$ -hydride elimination 234  
 iodides 222  
 iodine–magnesium exchange 71  
 iodoarenes 143  
 $ortho$ -iodobenzeneboronic acid 97  
 3-iodo-2-methyl-2-cyclohexanone 195  
 2-iodoxybenzoic acid (IBX) oxidations 513  
 ionization constant (pKa) 10  
 ionization equilibrium 9, 11  
 IPr-based catalysts 232  
 Ir-complexes of bioazoline (IBiox) 230  
 iridium catalyst system 416  
 iridium(I) complexes ([M]-halogen) 136  
 para-isomer 10  
 isomerization 55, 190, 469  
 – alkene 190  
 – of allylic boronate 409  
 – of corresponding allylboronate 55  
 – of  $\pi$ -allylpalladium intermediate 196  
 – of sec-alkylmetal intermediate 149  
 – stereochemical 143  
 isothioureas 369
- j*  
 JohnPhos 221, 222, 228
- k*  
 kanamycin (KA) 613  
 ketimines 420, 470, 581  
 – enantioselective allylation 421

- β-keto aryl and aliphatic ethers, reduction 584
- α-keto esters 461
- ketones
  - access via rhodium-catalyzed oxidative arylation 535
  - addition of allylic boronates to 93, 412, 413, 415, 419
  - addition reactions 412–417
  - allylation reaction 414
  - allylboration reactions, indium(0) catalysis 415
  - aromatic, catalyzed by spiroborate ester 583
  - catalyzing addition, of allylboronates to 414
  - chiral boronate in reduction 99
  - croylation reactions 413
  - crotylboration reactions catalyzed by a BINOL derivative 417
  - in DMSO/TFA demonstrated to give 464
  - *E*- and *Z*-crotylboronates copper-catalyzed addition to 413
  - as electrophiles 60
  - embedded within organoboron species 517
  - enantioselective 413
  - enantioselective reduction 28
  - in good yields, and with high enantioselectivity 286
  - with high diastereoselectivity 268
  - iridium-catalyzed ketone allylboration reaction 416
  - peptidyl 382, 383, 385
  - prochiral, 1,2-reduction of 581
  - to provide alketylboronates 68
  - *S*-Aryl-NHt-Bu thiosalicylamides, to form 382
  - unsaturated 300, 301, 305, 416
  - use of cationic palladium catalyst led to 465
  - using Shapiro reaction 45
  - via C–H activation/functionalization 90
- kinetic amine resolution
  - asymmetric direct amide formation 558
- I**
- β-lactamase inhibitors 104, 592
- β-lactones synthesis 575, 576
- Langmuir surface areas 660
- Lewis acid–allylboronate complexes 398
- Lewis acid-assisted Brønsted acid (LBA) 555
  - Ritter reaction catalyzed by 556
- Lewis acid-assisted Lewis acid (LLA) 567
- Lewis acid catalysis 395–403
  - benefits 405
  - catalytic allylboration, discovery 93, 395–397
  - chiral Lewis acids 400
- further developments 400–403
- mechanistic studies 397–400
- Lewis acid-catalyzed additions, with chiral allylboronates 403–407
  - *B*-chiral allylic boronates 403, 404
  - *C*-chiral allylic boronates 404–407
- Lewis acid-catalyzed allylboration reaction
  - diastereoselectivity 397
  - Lewis acidity 401
    - of boron 8
  - Lewis acids 1, 9, 393
    - acidity of boron in boronic acids 8
    - activation
      - in allylboration reaction 93, 396
      - of allylic boronates 397
      - of thiol ester 384
      - transition states with 398
    - of valine-derived oxazaborolidine 568
  - activator 303
  - for allylboronate additions to benzaldehyde 396
  - behavior of boronic acids 23
  - bis-Lewis Acid 584–586
  - Brønsted acid-assisted Lewis acid 570
  - with bulky chiral ligands 410
  - capable of coordinating basic molecules 9
  - as catalyst 394
  - catalyzed
    - additions with chiral allylboronates 403, 404
    - allylboration reactions 93, 395
    - reactions 403
    - chiral 28, 400
    - coordinated to oxygen atom of allylboronate 399, 400
    - for cycloadditions 28
    - diastereoselectivity 397, 401, 403
    - diol–Lewis acid complex 411
    - effect 401
    - Felkin selectivity 578
    - formal α-addition of allylic boronates to aldehydes 402
    - formation of intermediate carbocation 401
    - to generate acyliminium ions 545
    - Lewis acid-assisted Brønsted acid (LBA) 410, 555, 556
    - Lewis acid-assisted Lewis acid (LLA) 567, 569
    - mono-Lewis acids 586
    - multinuclear 628
    - *N*-acyl groups using 450
    - promoted
      - addition to aldehydes 407
      - conjugate addition of boronic esters to 92

- formation of reactive alkenyldifluoroborane intermediate 448
- reaction of alkynyltrifluoroborates with fluoroaziridines 544
- rearrangement of 2-fluoroaziridines 448
- reaction of 2-(1-alkynyl)arylaldimines and stannylnucleophile 446
- reversible Lewis acid–base interaction 636
- uses 400
- LFA-1 antagonist
  - asymmetric synthesis 563
- LiArB(OMe)<sub>3</sub> reagent 279
- Liebeskind–Srogl coupling 88, 369–371
- Liebeskind–Srogl desulfitative C–C cross-coupling reaction 88, 369
- ligand/Pd combinations 228
- ligand systems 269
  - bidentate phosphorus ligands 270–272
  - diene ligands 274, 275
  - mixed ligands 276, 278
  - monodentate ligands 270, 273, 274
- Lindlar’s catalyst 60
- linear boronate-linked materials 624
- linear boronate polymers 626, 627
- linear poly(boronate)s 627
- linear polymers 658
  - arising from transesterification 628
- lipid mixing experiments 612
- lipophilic trienylboronic acid 74
- lithiated enantioenriched styrene oxide 497
- lithium 2,2,6,6-tetramethylpiperazide (LTMP) 60
- lithium trimethylarylborate 268
- LUMO energy 623
  
- m**
- macrocycles 637
  - based on salicylideneamino alcohols, and arylboronic acids 651
  - subcomponent self-assembly 652
  - formed by 2,6-pyridinedimethanol and aryl boronic acid 650
- macrocyclic boronic esters 24, 637
- macrocyclic compounds 658
- macrocyclic structures 649
- magnesium bromide ( $MgBr_2$ ), addition 482
- magnetic resonance imaging (MRI) 603
  - low intrinsic sensitivity 603
- MALDI mass spectrometry 628
- maleimides 284
- malononitrile-substituted
  - organotrifluoroborate.
  - alkylation 511
- Mannich reactions 543–546
- Mannich-type reactions
  - boron-based (*See* Petasis reactions)
- mass spectrometry 77
- Mattheson asymmetric homologation 69
- Mattheson methodology 480
- melting points 76
- MeO-biphep 270
- (S)-MeO-biphep 270
- N-mercaptosuccinimides 387
- Merck–Banyu’s endothelin receptor antagonist 281
- mercury(II)-chloride 643
- metalated boronate compounds
  - with sugar motif 645
- metalated boronate macrocycles
  - based on dative bonds 645
- metalation 78, 79
- ortho*-metalation 41
- metal-based catalysts 419
- metal–boron bond
  - role in catalytic cycles 137
- metal-catalyzed additions
  - advances with organoboronic acids derivatives 455–471
  - copper-catalyzed oxidative addition 465–467
  - metal-catalyzed boration 467, 468
  - metal-catalyzed domino transformations 468–471
  - palladium-catalyzed additions 462–465
  - rhodium-catalyzed additions 455–461
- metal-catalyzed boration 467, 468
- metal-catalyzed borylation
  - of organic compounds 42, 43, 45, 135
- metal-catalyzed domino reactions 455
- metal-catalyzed domino
  - transformations 468–471
- addition reactions involving
  - imines 468–470
  - isocyanates 471
  - nitriles 470, 471
- metal-catalyzed protodeboronation 78, 79
  - silver nitrate-promoted 79
- metal–halogen exchange, and
  - cross-coupling 522–524
- metallic cyclic boronate compounds 643
  - synthesis 644
- metal–ligand interaction 644
- methacrylic resin solid-supported copper catalyst (MPI-Cu) 324
- methanol 350
- p-methoxybenzylation 256
- 3-methoxycarbonyl-5-nitrophenyl boronic acid 10

- methoxylation of tolylboronic ester 352, 353  
 methoxymethoxybenzene 40  
*p*-methoxyphenyl boronic acid 4, 5  
*p*-methoxyphenyl (PMP) group 466, 467  
*ortho*-methylamino-benzeneboronic acids 40  
 methylaquacobaloxime 644  
*N*-methylated cationic oxazaborolidine synthesis 574  
 methylboronic acid 13, 23, 222, 345  
 – oxidative cleavage 13  
 – use of methyl group 532  
*N*-methyl-boronopyridinium iodide 559  
 6-(3-methylbutyl)ylsulfonylpurine 364  
 methylcobaloxime 656  
*N*-methyldiaminoacetate 72  
 5,5'-methylene-bis(2-hydroxybenzencarbonyl) derivatives 652  
 methylenecyclopropanes (MCPs) 182, 197  
*N*-methyliminodiacetic acid (MIDA) 25, 252, 509  
 methyl ketones  
 – cyanosilylation 574  
 2-methyl-2,4-pentanediol esters 60  
*N*-methylpyrrolidinone (NMP) 553  
 $\alpha$ -methylstyrene 59  
 methyl thiopseudourea derivatives 368  
 MIDA adducts 25, 44  
 MIDA boronates 25, 72, 255  
 Mitsunobu reaction protocol 435  
 mixed ligands 276  
 monoalkylated cyclopentadienyl rhenium complexes 96  
 monoalkylboranes 30  
 monoarylboronate complex 605  
 – structure 606  
 monoborylation 135, 155  
 monoboryl complex 136  
 monodentate ligands 270, 273  
 monohydroxyborate ( $\text{ArBF}_2(\text{OH})^-$ ) 268  
 monosaccharides 23, 105, 607, 616  
 Mukaiyama aldol reactions 578, 579  
 Mukaiyama–Michael reactions 575, 577, 581  
 – of silyl ketene acetals 575  
 multicomponent reaction (MCR) 93, 96, 427, 436
- n**  
 (S)-( $-$ )-*N*-acetylcolchinol synthesis 484  
 natural products synthesis 437–442  
 N–B bond lengths 647  
 neomycin (NE) 613  
 neopentyl benzoate 41  
 neopentyl esters 41  
 networks 658–659  
 NHC-based catalysts 234  
 NHC ligands 155, 220  
 NHC–Pd precatalysts 233, 234  
 [Ni(acac)<sub>2</sub>] catalyst 364  
 nickel–carbene catalyst 90  
 nickel catalysts 91, 96, 141  
 – advantages 141  
 – boronic acid-thioorganic C–S desulfitative cross-couplings 364  
 – desulfitative C–C cross-coupling reactions with 364  
 – PCy<sub>3</sub>-based 204  
 – phosphine-free 190  
 – selectively afforded germaborative dimerization product 208  
 – silaborative C–C bond cleavage reaction 199  
 – with/without phosphorus ligands 203  
 nitriles 40, 81, 235, 455  
 – addition reactions involving 470  
 – arylation of 461  
 –  $\alpha,\beta$ -unsaturated 180, 181  
 – Pd(II)-catalyzed arylation 464  
*ortho*-nitrobenzeneboronic acid 10  
 nitrogen–oxygen heterocycles 3  
 NMR spectroscopy 77, 415, 420  
 nonchiral boron-based catalysis 551–561  
 – aldol and Biginelli reactions 560, 561  
 – amide condensation 551–558  
 – esterification reactions 559, 560  
 nonpolar recrystallization solvents 74  
 2,5-norbornadiene (nbd) 269  
 nuclear magnetic resonance spectroscopy 77, 78  
 nucleophilic organometallic reagents 263  
 nucleophilic substitution  
 – on boron atom 171  
 – mechanism 57
- o**  
 O’Brien’s (+)-sparteine surrogate 486  
 (S)-3,3’-(3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>-5,5’,6,6’,7,7’,8,8’-octahydro-BINOL ligand 445  
 oligoarenes 73  
 oligo(boronic acid) metallic duplexes 649  
 oligomeric anhydrides 1, 15  
 oligophenylene 254  
 oligosaccharides 25, 102, 103, 610, 647  
 one-pot sequential Diels–Alder cycloaddition/amidation 556  
 organic azides, treatment with organodichloroboranes 540

- organobis(diphenylglyoximato) cobalt(III)  
complexes 644
- organobismuth reagents 354
- organoboron compounds 534
- electrophilic functional groups incorporated within 510
  - oxygen-containing 2
  - preparation of 148
  - role 428
- organoboronic acids 135
- *N*-acyliminium ions reactions with organoboronic acids derivatives 449–455
  - addition 472
  - dehydration of 266
  - metal-catalyzed additions
    - advances with organoboronic acids derivatives 455–471
  - nucleophilic addition reactions, recent advances in 396–473
  - palladium-catalyzed addition reactions 455
  - Petasis Borono–Mannich reaction, recent advances in 428–449
  - stereoselective Rh(I)-catalyzed additions 458
  - transmetalation of 265
- organoboronic esters 16, 135, 254
- organoboron reagents 263, 385
- aryl- and alkenyl-derived 455
  - competent in Rh-catalyzed enantioselective conjugate additions 268
  - nature of 295
  - organoboron sources 266
  - Pd-catalyzed enantioselective conjugate addition 299
  - stoichiometry of 266
  - $\alpha,\beta$ -unsaturated phenyl sulfones react with 289
- organoboroxines 15, 266
- organometalloids 354, 355
- organophosphines 217–219, 221
- as ligands in the Suzuki–Miyaura reaction 216
- organo-SOMO catalysis 449
- organostannanes 367, 373
- organotrifluoroborate reagent
- $\alpha$ -carbon 452
- organotrifluoroborates 30, 513
- 1,2-addition reactions 534, 535
  - 1,4-addition reactions 535, 536
  - amination and amidation reactions 540–542
  - carbon–carbon bond-forming reactions
    - with activated electrophiles 542–546
  - catalytic hydrogenation reactions 514, 515
- C–H activation 536, 537
  - characteristics 515
  - cross-coupling reactions 526–534
  - Diels–Alder reactions 525, 526
  - elaboration via transformations, of pendant functional groups 509–526
  - Huisgen dipolar cycloadditions 520–522
  - hydroboration reactions 524, 525
  - hydrolysis reactions 538, 539
  - Mannich reactions 543–546
  - metal–halogen exchange and cross-coupling 522–524
  - oxidation reactions 511–514
  - reactions with oxocarbenium ions 542, 543
  - reductive amination reactions 515–517
  - substitution reactions 510, 511
  - syntheses 30, 509
  - synthetic approaches to 508, 509
  - TosMIC condensation reactions 520
  - transition metal-catalyzed processes 526–537
  - Wittig and Horner–Wadsworth–Emmons reactions 517–520
- organotri-*n*-butylstannanes 377
- organozirconium reagents 205
- orthogonal chemistry 373, 374
- orthogonal transformations, protection of boronic acids for 72
- oxacalix[2]arene[2]pyrimidines 372
- oxa- $\pi$ -allylrhodium 265
- oxazaborolidines 40, 99
- 1,3,2-oxazaborolidines preparation 584
- oxazaborolidinone catalysts 26, 577–581
- Diels–Alder reactions 578, 579
  - Mukaiyama aldol reactions 578
  - Mukaiyama–Michael reactions 577, 578
- oxazaborolidinone/substrate complexation studies 579–581
- oxazaborolidinones 26
- 1,3-oxazolidin-2-thiones (OZT) 370
- 1,3-oxazoline- (OXT) 370
- Liebeskind–Srogl cross-coupling conditions 370
- oxidation reactions 79, 511–514
- oxidative replacement, of boron 79
- amidation 81
  - amination 81
  - oxygenation 79–81
- 3-oxo alkylboron pinacolates 72
- 3-oxo-(*E*)-1-alkenylboronates 60
- oxyacid 9
- $\beta$ -oxy-boronic ester synthesis 499

**p**

- palladacycles
  - of arylboronic acids to  $\alpha,\beta$ -unsaturated carbonyls 303
  - as catalysts for conjugate addition of organoboronic acids 303
- palladium catalysts 195
  - based on SPhos 88
  - bearing chiral monodentate phosphine 194, 195
  - benzyl chlorides and bromides, borylated with  $B_2Pin_2$  148
  - cascade reactions 305
  - coupling of  $\alpha$ -amino thiol esters, with organostannanes 377
  - cross-coupling reactions 2
  - cyclization reaction 88
  - dehydrogenation/C–H borylation sequence, borylated with 157
  - generated *in situ* from  $Pd(OAc)_2$  with 187
  - inactive 192
  - for monoborylation/diborylation of alkenes and alkynes 135
  - palladium-catalyzed silaboronation of allenes 59
  - palladium ligand systems 42
  - promote addition of silylboranes 188
  - regioselectivity of diboration of terminal allenes 178
  - thiol esters and boronic acids crosscoupling 366
  - trialkylstannylpinacolborane used with 207
  - use of cationic 465
  - variant 97
- palladium-catalyzed addition reactions 462–465
  - arylation of imines 462, 463, 464
  - chiral N-sulfinylimines, diastereoselective arylation and alkenylation of 463, 464
  - imines, enantioselective arylation 464
  - isocyanates, arylation 465
  - nitriles arylation 464, 465
- palladium-catalyzed cross-coupling reactions 527
- palladium–thiolate bond 379
- paracyclophane derivative 28
- Pd-catalyzed enantioselective conjugate addition
  - to  $\alpha,\beta$ -unsaturated esters, amides, and aldehydes 304–306
  - to  $\alpha,\beta$ -unsaturated ketones 300–304
  - of arylboronic acids to  $\beta$ -arylenones 302
  - of organoboronic acids

- to  $\beta$  aryl enals 305
- to  $\alpha,\beta$ -unsaturated esters and amides 304
- of organoboron reagents 299, 300
- Pd-catalyzed intramolecular carboboration 60
- $Pd_2(dbu)_3$ /triethylphosphite 375
- Pd(II)-catalyzed process 537
- $Pd(PPh_3)_4$ -catalyzed catecholboration 58
- pentaerythritol 626, 627, 637
- pentameric macrocyclic structures 654
- 1,2,2,5,5-pentamethylpiperidine 351
- peptidic S-acylthiosalicylamides 383
- peptidic thiol esters 377
- peptidyl ketones 382, 383
- Petasis borono-Mannich reaction 93, 96, 427–431, 428, 435–438, 442, 447, 450, 453, 466, 472, 543, 544
- aminocyclization route 433
- catalytic enantioselective reactions 431
- with chiral branched amines 433
- combinatorial and solid-phase synthesis, applications in 434–437
- computational analysis 442–444
- feature 429
- mechanistic routes for 429
- microwave accelerated reactions 430
- natural products and pharmacological agents
- application toward synthesis 437–442
- Petasis reaction variants 444–449
- recent advances in 428–449
- solvents and additives 430, 431
- substrate scope 431–434
- Petasis-like reaction
  - 2*H*-chromenes formation 447
- PF-FB structure 601
- PF1 oxidation, by  $H_2O_2$  599
- pharmaceuticals 153, 222
- phase-switch synthesis 64–65
- (*S*)-3,3'-Ph<sub>2</sub>-BINOL catalysis 421
- 9,10-phenanthrenequinone 97
- phenyl–boron–phenyl assembly 627
- phenol 10, 14, 42, 64, 79, 94, 97, 269, 320, 342
  - arylboronic acid is oxidized to 80, 351
  - formation 351
  - impurity 269
  - source of phenol by-product 352
- phenolic methoxymethyl ether 14
- phenylalanine-derived thiol ester 385
- phenylborinic acid
  - Biginelli three-component condensation catalyzed 563
  - catalyzes direct aldol reactions of pyruvic acids 561

- phenylboronic acid 3, 4, 8, 14, 24, 27, 97, 99, 269, 647  
 – arylation of cyclic thiourea at sulfur 346  
 – binding equilibrium 592  
 – binding equilibrium with diol 592  
 – catalyst for the Biginelli reaction 561  
 – characterization 77  
 – chiral diene ligands 275  
 – condensation  
 –– with 2,6-pyridinedimethanol and 2-(salicylideneamino)-1-hydroxyethane 647  
 – diastereoselectivities 470  
 – diazonium salts 611  
 – enantioselective addition to  $\alpha$ -acetamidoacrylic esters 291  
 – functionalization 611  
 – Petasis borono-Mannich, reaction profile 444  
 – 4-phenylbutyric acid and benzylamine catalyzed by 557  
 – as protecting group for 99  
 – toxicity 103  
 – x-ray crystal structure 3  
*N*-*m*-(phenylboronic acid)-2,2'-bipyridine-5-carboxylamide 645  
 phenyl–boron–phenyl sandwiches 622  
 1,4-phenyldiboronic acid 44, 639  
*para*-phenyl diboronic acid 660  
*ortho*-phenyldiboronic ester 12  
 5-phenyl-3,4-dihydropyrimidin-2-one 367  
 1,4-phenylenebisboronic acid 44, 656  
 1,2-phenylenediamine 27, 28  
 phenylene-1,3-diboronic acid 44, 639  
 phenylene-1,4-diboronic acid 44, 626  
 2-phenyl-ethylboron derivatives 150  
 phenylrhodium 264, 265  
 2-phenyl-4,4,5-tetramethyl-1,3,2-dioxaborolane 3  
 phorbol myristate acetate (PMA) 603  
 phosphine ligands 135  
 phosphine oxide, containing polymers 627  
 phosphine sulfide, containing polymers 627  
 phosphinite/phosphite-based palladacycle-catalyzed arylation 462  
 phosphite-based  $\pi$ -acidic palladacycles 462  
 phosphoramidites 265  
 pinacol 3, 17, 20, 60, 205, 539  
 pinacol alkenylboronates 71, 143  
 pinacol allylboronate 399  
 – addition 396  
 – CuF–DuPHOS-catalyzed addition 420  
 – indium-catalyzed addition 414  
 – nickel-catalyzed addition 402  
 pinacol arylboronates 70, 71  
 pinacolborane 25, 42, 55–58, 61, 135, 186, 205  
 – derivatives 205  
 pinacol boronic esters 17, 19  
 – homologation, styrene oxide for 499  
 pinacol 1-phenylethylboron derivatives 150  
 pinanediol phenylboronic ester 22  
 pivaloylaniline 40  
 planar bipyridine ligand 160  
 platinum catalyst 193  
 platinum-catalyzed alkyne diboration 176  
 PL1 structure 602  
 polarizable continuum model (PCM) 443  
 poly(anilineboronic acid) (PABA) 631, 633  
 – monomer synthesis 632  
 polyaryls 143  
 poly-3',6'-bis(1,3,2-dioxaborinane) fluoran 628  
 poly(boronate)s incorporating metal 629  
 polycenyl MIDA boronate esters 255  
 polyglycerol 76  
 polyhydroxylated alkaloid natural products synthesis 442  
 poly(L-lysine) 633  
 – binding of saccharides 634  
 polymerizations  
 – atom transfer radical 633  
 – based on Suzuki coupling reactions 621  
 – of boron 622, 623, 630  
 – molecular imprinting 102  
 – prone ethyleneboronic acid 45  
 – radical 595, 633, 666  
 – reversible addition–fragmentation chain transfer (RAFT) 635, 636  
 – tubulin 103, 592  
 poly(olefin)s 622  
*N*-polystyrene-bound 4-boronopyridinium chloride 553, 554, 560  
 polystyrene-*co*-4-vinylpyridine (PS/4-VP) 636  
 polystyryl boronic acid 102  
 poly(uracil) 630  
 p-orbital of boron 6  
 positron emission tomography (PET) 30, 605  
 postpolymerization modification of precursor polymers 630  
 potassium alkenyltrifluoroborates 30, 447, 529  
 potassium alkynyltrifluoroborates 531  
 potassium aminomethyltrifluoroborates 532  
 potassium aryltrifluoroborates 348, 527  
 potassium (*Z*)-2-chloroalk-1-enyltrifluoroborates 529  
 potassium organotrifluoroborates 30, 526  
 – organocatalytic 1,4-addition 451

potassium organotrifluoroborate salts  
     30, 268  
 potassium 2-pyridine triolborate 342  
 potassium 3-pyridine triolborate 342  
 potassium 2-substituted-1,3-  
     dithianotrifluoroborate reagents 451  
 prochiral ketones  
     – Corey–Bakshi–Shibata (CBS)  
         reduction 567  
 proline-derived oxazaborolidine 573  
 proteasome inhibitor 104, 467, 595  
*N*-protected peptidyl ketones 375  
*N*-protected/substituted isothiourea  
     systems 369  
 protein labeling 106  
 protic acid catalysis 409, 411  
 protodeboronation 14, 70, 78, 266  
 protolytic deboronation 14–15, 78  
 PR1 structure 602  
 Pt(O) catalyst 59  
 purines 326–329  
 PX1 structure 602  
 pyrazine 97  
 pyrene-2,7-diboronic acid (PDBA) 663  
 pyridine complexation 12  
 2,6-pyridinedimethanol 643, 647, 650  
     – macrocycles formed by 650  
 pyridinium dichromate (PDC) oxidation  
     486  
 2-pyridinylboronic acid 44, 342,  
     367, 368  
 3-pyridinylboronic acid 342, 644  
 4-pyridinyl boronic acid 378, 644  
 3-pyridylboronic acid 644  
 pyrimidinones 373  
 pyrimidinyl arylglycines  
     – synthesis 436  
 2-pyrimidinyl-substituted alkenyl sulfide  
     378  
 2-pyrimidyl vinyl sulfide 378  
 pyrrolidine-containing arylglycines  
     – diastereoselective synthesis 431  
 pyrrolidine ring formation  
     – Petasis borono-Mannich/ring-closing  
         metathesis (RCM) approach 439  
 pyruvic acids 561  
     – direct aldol reaction 563

**q**  
 quantum mechanical (QM) calculation 659,  
     660  
 quaternization, of arylboronic acid 265  
 8-quinolineboronic acid 97  
 quorum sensing process 592

**r**  
 ratanhine 255  
 ratiometric fluorescent sensors  
     – use of 602  
 reactions, with oxocarbenium ions 542, 543  
 reactive oxygen species (ROS) 107, 597  
 recrystallization 29, 74  
 reductive amination reactions 515–517  
 regioselective Diels–Alder reaction  
     – hypothetical transition states in 571  
 reverse-phase HPLC chromatography 77  
 reversible addition–fragmentation chain  
     transfer (RAFT) polymerization 635  
     – of boronic acid acrylamido monomers 636  
 $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$  269  
 $[\text{Rh}(\text{Ar})(\text{S})\text{-binap}]$  intermediate 266  
 $[\text{Rh}(\text{nbd})_2]^+\text{BF}_4^-$  complex 269  
 Rh-catalyzed enantioselective conjugate  
     addition 90  
     – applications 293  
     – of arylboronic acid on  $\beta$ -aryl  $\alpha,\beta$ -unsaturated  
         esters 280  
     -- synthesis of endothelin receptor  
         antagonists 281  
     – of arylboronic acids to arylmethylene  
         cyanoacetates 288, 289  
     – of arylboronic acids to enals 279  
     -- reaction pathways 278  
     – to 2,3-dihydro-4-pyridones 282  
     – to diphenylphosphinylallenes 294  
     – of ester in synthesis of APIs 280  
     – ligand control of the selectivity 279  
     – to maleimides 285  
     -- influence of ligand on regioselectivity 285  
     – of organoboronic acid to  $\alpha,\beta,\gamma,\delta$ -  
         diunsaturated esters 295  
     – of organoboronic acid with alkenyl  
         sulfones 290  
     – with other organometallic reagents 296,  
         297  
     – of  $\text{PhB}(\text{OH})_2$  to *N*-benzylmaleimide  
     -- activity and selectivity of different  
         ligands 285  
     – of phenylboronic acid to di-*tert*-butyl  
         fumarate 284  
     – with (pin)B-SiMe<sub>2</sub>Ph 287  
     – in synthesis of core platensimycin 287  
     – synthetically useful acceptors in 286  
     – using guaiacol 292  
 $[\text{Rh}]$ /diene catalytic system 283  
 rhodium(I) tricarbonyl complex 96  
 Rh(I)-imine complex 461  
 Rh/ligand catalytic systems 287  
 $[\text{Rh}(\text{m-OH})(\text{nbd})_2]$  269

- [Rh(m-OH)(cod)] 265  
 [Rh(m-OH)(cod)]<sub>2</sub> 269  
 [Rh(m-OH)(R)-binap]<sub>2</sub> dimer 265  
 rhodium catalysts 43  
 – catalytic hydroboration use of 171  
 – change chemoselectivity 171  
 – chiral 61  
 – higher reactivity in diboration of alkenes with B<sub>2</sub>cat<sub>2</sub> 177  
 – phenylboronic acid deactivate chiral diene rhodium catalysts 269  
 – reactions 536  
 – Rh-catalyzed enantioselective conjugate additions 90, 263  
 – tandem processes 297  
 rhodium-catalyzed addition reaction 91, 455–461  
 – arylation of imines 455–456  
 – 1-arylethenyl acetates 90  
 – β,β-disubstituted α,β-unsaturated ketones 268  
 – boronic acids onto carbonyl compounds 91  
 – chiral N-sulfinylimines, diastereoselective arylation and alkenylation of 456–458  
 – imine derivatives 91  
 – imines, enantioselective arylation 458–460  
 – isocyanates, arylation and alkenylations 461  
 – nitriles and cyanoformates, arylation 461  
 rhodium–diene complexes 265  
 rhodium/diphosphine catalytic systems 298  
 Rh-phosphine complex 269  
 Rh precatalysts 269  
 Rh/(S)-binap system 279  
 Ritter-type amidation reaction 540  
 ROMP gel diol 76  
 rotaxanes 90, 658, 660
- s**
- saccharides  
 – binding to poly(L-lysine) 634  
 – biologically important 608  
 – determination of 25  
 – diaza-18-crown-6-based saccharide receptor 647  
 – boronate complex based on 650  
 – guests 647  
 – oxidative cleavage 433  
 – polyfunctional 633  
 – polysulfated 103  
 – receptors 102  
 – regioselective sulfation 99  
 2-(salicylideneamino)-1-hydroxyethane 647  
 salicylaldehyde imines 97  
 s-BuLi 40, 481, 489, 493  
 Schrock carbene 71  
 selective transformations, on protected boronic acids 73  
 sensing system 614  
 sequential Diels–Alder cycloaddition/amidation reaction 557  
 sialic acids  
 – structures 604  
 – synthesis  
 -- Petasis borono-Mannich reaction 443  
 side-chain-functionalized boronate materials 630–637  
 side-chain organoboron materials 630  
 [3,3]-sigmatropic rearrangement 401  
 silaboration 185  
 – alkenes 191–200  
 – alkynes 187–191  
 – allenes 191–200  
 – benzylidenecyclopropane 197  
 – bicyclopolylidene 198  
 – cyclic 1,3-dienes 192  
 – 1,3-cyclohexadiene 193  
 – cyclohexylidenecyclopropane 198  
 – 1,3-dienes 191–200  
 – methylenecyclopropanes 191–200  
 – silaboration products, synthetic application 200–202  
 – silylborane reagents 185–187  
 – of unsaturated compounds 59  
 silica gel chromatography 74  
 silica gel protocol 539  
 silicon–silicon bonds 171  
 siloxane [t-BuSi<sub>3</sub>Si-t-Bu] 640  
 α-silylallylboronate 60  
 β-silyl borane 490  
 silylborane Et<sub>3</sub>SiBpin 155  
 silylboronic acid derivatives 185  
 (silyl)(4-borylallyl)platinum intermediate 193  
 silyl enol ethers 26  
 silyl ketene acetals  
 – Michael reaction, development 575  
 – Mukaiyama–Michael reactions 575  
 β-silyl (E)-vinyl-(9-BBN) borane 489, 490, 492  
 SmithKline Beecham's endothelin receptor antagonist 281  
 sodium dodecyl sulfate (SDS) 462  
 sodium methylsulfinate 347  
 sodium phenylsulfinate 347  
 sodium triacetoxyborohydride (STAB) 515  
 solid-phase synthesis 374, 375  
 – applications in combinatorial and 434  
 – Chan–Lam cross-coupling in 324  
 – of peptidomimetics 428

- transition metal-catalyzed 374
- solid-supported diol resins 76
- solvent system 553
- Sonogashira cross-couplings 256, 374
- Soxhlet extraction 508, 516
- SPhos 88, 224–228
- spiroborate catalysts 581–584
- (E)-benzyl oxime ethers, 1,2 reduction 583, 584
- prochiral ketones, 1,2-reduction 581–583
- SPR experiments 613
- stannanes
  - as allylating reagent 413
  - transmetalation 41, 42
- Stemona alkaloids 453
- pyrido[1,2-*a*]azepine core synthesis 453
- stereochemical model 266
- steric hindrance 160
- streptomycin (ST) 613
- (E)- $\beta$ -styryl-boronic acids 375, 441
  - Petasis borono-Mannich cyclization 433
- 1-substituted-1-alkenylboronate 58
- 2-substituted 1-alkynylboronic esters 43
- ortho*-substituted boronic acids 41
- 1-substituted cyclopentadienes
  - Diels–Alder adducts 571
- 1- and 2-substituted cyclopentadienes
  - regioselective Diels–Alder reactions 570
- substitution reactions 510, 511
- N*-sulfinylimines
  - diastereoselective arylation and alkenylation 456, 463
  - Rh(I)-catalyzed additions, rationale for stereoselectivity 457
- sulfones
  - in desulfurative nickel-catalyzed cross-coupling reactions 364
  - as substrates 364
- sulfonium salts 365
  - as substrates 365, 366
- sulfonylaldimines
  - arylation using chiral phosphoramidite ligands 460
- N*-sulfonylated amino acids 26
- sulfonyl chlorides 365
- supramolecular boronate assemblies 629, 630, 653–655, 667–671
- supramolecular interactions 658
- surface covalent organic framework (SCOF-1) 664
- surface plasmon resonance (SPR) analysis 613
- Suzuki–Miyaura cross-coupling reactions 14, 31, 41, 60, 85, 87, 214, 471, 515, 527, 529, 531, 533, 615
  - asymmetric 241, 242
  - achieving axial chirality 241–246
  - achieving point chirality 246–248
  - of challenging aryl halides 85, 220
  - coupling of carbocyclic substrates 221–222
  - coupling of heterocyclic substrates 222–224
  - low catalyst loadings 226–228
  - organophosphine-derived catalysts 221, 222
  - overview of challenges 220
  - in water 224, 226
  - involving unactivated alkyl halides 234
  - associated difficulties 234
  - coupling of secondary alkyl halides 237–240
  - cross-coupling-promoted NHC ligands 240, 241
  - cross-couplings of primary alkyl halides 235–237
  - iterative 72, 249
  - iterative cross-couplings via orthogonal reactivity 72, 249–256
  - *ortho* metalation–cross-coupling iterations 248
  - triflating–cross-coupling iterations 248, 249
  - at low loadings of Pd in presence of organophosphines 219
  - mechanistic aspects 85, 214, 215
  - catalytic cycle 215
  - NHC-derived catalysts 228
  - *in-situ*-generated catalysts from imidazolium salt precursors 228–231
  - preformed NHC–Pd complexes 231–234
  - *N*-heterocyclic carbene ligands 88, 220
  - organophosphine and NHC ligands 220
  - rational design of ligands 215–217
  - organophosphine ligands 217
  - selection of imidazolium salts and NHC–Pd complexes 218
  - (–)swainsonine synthesis 439, 441
  - synthetic approaches, to
    - organotrifluoroborates 30, 508, 509
    - synthetic lectins 25
- t**
- Takai reaction 60
- Tamao oxidation 202

- tandem carborhodation/conjugate addition 298, 299
- tandem 1,1-carborhodation/conjugate addition 299
- tandem enantioselective conjugate addition/  
Aldol reaction 297, 298
- tartratic acid-derived boronate ester TarBNO<sub>2</sub>/  
NaBH<sub>4</sub> system 586
- applications 587
- tartramide-derived dioxaborolane 99
- tartrate esters 27
- Tb-DTPA-(EN)<sub>2</sub> 604, 605
- Tb-DTPA-(ENPBA)<sub>2</sub> 604, 605
- Tb-DTPA-(PBA)<sub>2</sub> 604, 605
- Tb-DTPA system 604, 605
- t-butoxycarbonyl groups 14
- tertiary boronic esters 497
- tetraalkoxydiborons, for catalytic diboration 173
- tetraamide ligand 605, 606
- tetrabutylammonium difluorotriphenylsilicate (TBAT) 414
- tetrabutylammonium fluoride (TBAF) 414
- tetracoordinate boron complex 429
- tetracoordinate organoboron 429, 507
- tetrahedral character (THC) value 647
- tetrahedral hydroxyboronate 25
- tetrahydrofuran 14
- tetrahydroquinolines 470
- 1,2,4,5-tetrahydroxybenzene 627, 639, 661
- tetrameric boronate macrocycles 654
- N,N,N',N'*-tetramethylethylenediamine 640
- 2,2,6,6-tetramethylpiperidine (LTMP) 41
- 2,2,6,6-tetramethylpiperidine 447
- tetramethylrhodamine-boronic acid (TMR-B) 609
- tetra-*n*-propyl perruthenate (TPAP) catalyzed reactions 513
- tetraserine-containing proteins 106, 616
- TF antigen
- peptidyl bisboroxole 611
  - structures 611
- thallium alkoxides 531
- Th1 and Th2 cells signaling pathway 438
- thioalkynes 58, 368
- thioamides as substrates 369–371
- thioether–boronic acid cross-coupling reactions 88, 369
- thioethers 370
- and related substrates 88, 368, 369
- thiol ester–boronic acid cross-coupling 88, 384
- thiol ester–boronic acid desulfitative coupling 367
- thiol esters 366, 385
- as substrates 366–368
- thioorganic–boronic acid coupling 379
- thioorganic partners, participate in desulfitative functionalization 372
- thioureas
- catalyst 454
  - as substrate 369–371
- Thomsen–Friedenreich (TF) disaccharide antigen 610
- TMSCl protocol 538
- TMSCN 574
- ortho*-tolylboronic acid 10
- para*-tolylboronic acid 14, 254
- tolylboronic ester
- Cu-catalyzed methoxylation 353
- N*-tosylarylimines 91
- N*-tosyl/*N*-benzenesulfonylarylaldimines
- palladium-catalyzed arylation 462
  - tosylmethyl isocyanide (TosMIC) 520
  - condensation reactions 520
  - formyl-substituted organotrifluoroborates condensation 521
- trans*-alkenylboronic acids 58
- transannular Diels–Alder (TADA) reaction 568, 569
- transesterification, with diethanolamine 22
- trans*-hydroboration 58
- transition metal catalyzed bis-silylation 171
- transition metal-catalyzed carbon–sulfur bond formation 387
- transition metal-catalyzed processes 526–537
- transition metal-catalyzed transformations
- of boronic acids (esters) 89, 90
- transition metals 79, 273
- transition state energy
- calculation 399
- transmetalation 78, 135, 136
- of arylsilanes and arylstannanes 32
  - from boron to copper 384
  - from boron to rhodium 266
  - between B<sub>2</sub>pin<sub>2</sub> and CuOAc 137
  - to Cu 379
  - of organoboronic acids 78, 265
  - process by polarizing Pd-thiolate bond 380
  - with [Rh(m-OH)(cod)] 265
  - thallium alkoxides, to facilitate 531
- transmetalation–protodeboronation of boronic acids 79
- transmetalative acylboration of allenes 205
- transmetalative carboboration 205
- utilizing organozirconium reagents 206

trialkylphosphines 217  
 trialkylsilanes 158  
 triarylboronamide 254  
 1,2,5-triazepine-3,7-diones synthesis 439  
 triazolo-substituted systems 521  
 $\alpha,\alpha,\alpha$ -trichloroaldimines 543  
 tricoordinate boron reagents, instability 507  
 tricoordinate organoborons, limitations 509  
 tricyclohexylphosphine 42  
 triethylborane 1  
 triflic acid 305  
 3,4,5-trifluorobenzeneboronic acid 97  
 trifluoroborates 30, 341  
 – characteristics 538  
 trifluoroborate salts 20, 30, 31, 64, 72, 338, 340  
 trifluoromethylbenzene 161  
 trihydroxyborate salts 30  
 2,4,6-tri-i-propylbromobenzene 228  
 4,4,6-trimethyl-1,3,2-dioxaborinane 25  
 trimethylsilylate 633  
 3-trimethylsilyl indazoles 325  
 $\alpha$ -trimethylsilylmethylboronic ester 60  
 $\alpha$ -trimethylsilylmethyl pinanediol  
 allylboronate 406  
 – chiral  $\alpha$ -substituted double-allylation  
 reagent 406  
 tri-*n*-butylphenylstannane 374  
 (triorganosilyl)boronic ester  
 – for catalytic silaboration 186  
 – synthetic routes to 185  
 trisboryl complex 136  
 trisubstituted alkenes synthesis  
 – potassium alkyltrifluoroborate, cross-  
 coupling 529  
 1,2,3-trisubstituted 1*H*-3-indenamines  
 synthesis 468  
*tropos* biphenyl backbone 272  
 troxylhydrazones 96  
 tunable catalysis 373

**u**  
 Ullmann–Goldberg reaction 315  
 umbelliferone 601  
 (–)-uniflorine A structure 439, 440  
 $\alpha,\beta$ -unsaturated aldehydes 278  
 $\alpha,\beta$ -unsaturated esters  
 – Rh-catalyzed enantioselective addition  
 to 279, 280  
 – synthesis of APIs 280  
 unsaturated heterocycles 3

$\alpha,\beta$ -unsaturated ketone 305  
 unsaturated organotrifluoroborates  
 – dihydroxylation 512  
 $\alpha,\beta$ -unsaturated unsaturated ketones 263  
 – model for enantioselection 266  
 – rhodium-catalyzed enantioselective  
 conjugate addition 264  
 – mechanistic cycle 264  
 Upjohn process 512

**v**

vaulted biphenanthrol ligand (VAPOL) 561  
 Velcade (bortezomib) 2, 104, 105, 467, 469, 479, 480  
 $\alpha$ -vinylation  
 – of aldehydes 449  
 – of carbonyl compounds 95  
 $\alpha$ -vinylation 337  
 – using Chan–Lam chemistry 336  
 $N$ -vinylation of azoles 339  
 $\alpha$ -vinylation of carbonyl compounds 95  
 vinylcyclopropanes (VCPs) 199  
 $(E)$ -vinyl neopentyl glycol boronic esters 489  
 vinyloxysilanes, [2+2] cycloaddition  
 reactions 573  
 4-vinylphenyl boronic acid 641  
 vinyl tert-butyl sulfones 364  
 vitamin C 595  
 – negative effect 596  
 Vivol-SnCl<sub>4</sub> catalyst system  
 – aldehyde allylation, general conditions  
 for 411  
 – X-ray crystal structure 411

**w**

Wiberg indices 444  
 Williamson ether protocol 542  
 Wittig reactions 517–520

**x**

XPhos 224, 225  
 X-ray crystallographic structure  
 – boronic acid derivatives 3  
 – bond distances 5  
 – of phenylboronic 4  
 – of trihydroxyboronate salt 9

**z**

Zimmerman–Traxler-type transition state  
 model 393, 397, 470  
 zwitterion 11

