

## Index

### a

- acid-and base-catalyzed reactions 328–333
- aerobic oxidations, with polyoxopalladates 16–17
- AIM method 178
  - bonded interaction nature 189–190
  - working of 187–189
- alkane
  - hydroxylation 39
  - oxidation 40
- alkene 29, 153, 154, 155, 157–161
  - epoxidation 30–31, 33–34
  - oxidation 32, 35, 36, 37
- allenes 195
  - aminoallenes cyclization 203–205
  - hydroxyallenes cyclization 196–203
  - synthesis 252
  - thioallenes cyclization 206
- allylic sulfinylation, palladium-catalyzed 67, 68, 69
- allyl sulfoxides, aromatic sulfinylation from 72
- amides 259, 265, 266, 267, 269, 270, 271
- amino acids 131–132, *see also* bicyclo[2.2.2]octenes
- aminoallenes cyclization 203–205
- anilides cyclization 220–221
- arenes
  - direct alkenylation of 216
  - direct arylation of 218–219
  - direct (hetero)arylation of 215
- arenesulfenic acid, calixarene-tethered 51
- aromatic sulfinylation 69
  - from allyl sulfoxides 72
  - palladium-catalyzed
    - enantioselective 70
    - halide recognition in 70
- N-aryl  $\beta$ -enaminones cyclization 221–223
- Ascohyllum nodosum* 95
- asymmetric aldol reactions 333–334
- asymmetric catalysis, *see* imidates; Nozaki–Hiyama–Kishi reaction development
- asymmetric hydrogenation 153, 154, 155, 156–158, 157, 160, 161, 162, 163
- atom in molecule (AIM) method 178
- aziridination 258, 259–260, 264–265, 268–269, 272, 274

### b

- back donation 187
- ball mills 327
  - acid-and base-catalyzed reactions 328–333
  - metal-catalyzed reactions 338
    - CU-catalyzed reactions 343–345
    - miscellaneous 345–347
    - Mizoroki–Heck reaction 340–341
    - Sonogashira reaction 341–343
    - Suzuki–Miyaura reaction 338–340
  - organocatalytic methods 333
  - asymmetric aldol reactions 333–334
  - cycloaddition and related reactions 335–338
- basis sets 172–174
- benzenesulfenic acid sulfinyl precursors
  - preparation and thermolysis 54
- bicyclo[2.2.2]octenes 131–133
  - DDAA derivatives and 133
  - homogeneous hydrogenation and hydrogenolysis reactions with dehydroamino acid derivatives and 136
  - nanometal colloids modified catalysts 136–140
  - nanooxide colloids-modified catalysts 140–142
- hydrogenolysis

- bicyclo[2.2.2]octenes (*contd.*)
  - – heterogeneized ligand-modified nanoclusters 142–144
  - layered-double hydroxides, as support for Rh(TPPTS)<sub>3</sub> and Rh(*m*-TPPTC)<sub>3</sub> homogeneous catalysts 144–147
  - ligands 133, 135–136
- BINOL 335
- biocatalysis, *see* hydrogen peroxide
- bioinspired oxidations, catalyzed by nonheme iron and manganese complexes 27
  - *cis*-dihydroxylation
    - – iron-based catalysts 34–37
    - – manganese-based catalysts 37–38
  - desaturation
    - – iron-based catalysts 41–42
    - – manganese-based catalysts 42–43
  - epoxidation
    - – iron-based catalysts 27–30
    - – manganese-based catalysts 30–34
  - hydroxylation
    - – iron-based catalysts 38–39
    - – manganese-based catalysts 40–41
- bond dissociation energy (BDE) 260
- C**
  - Caldariomyces fumago* 93
  - Candida antarctica* B 94, 96
    - carboxylic acids 37
  - catalyst precursors 112–117
  - catalyst–substrate adducts 107, 122, 124, 126
  - catalytic oxidation, *see* bioinspired oxidations, catalyzed by nonheme iron and manganese complexes
  - C–C bond-forming reactions
    - via aryl-h addition to terminal alkynes 223
    - via (hetero)aryl-H/Ar<sub>2</sub>I<sup>+</sup>X-coupling 217–219
    - via (hetero)aryl-H/R-X coupling 212–216
  - C=C bonds catalytic oxidation
    - *cis*-dihydroxylation
      - – iron-based catalysts 34–37
      - – manganese-based catalysts 37–38
    - epoxidation
      - – iron-based catalysts 27–30
      - – manganese-based catalysts 30–34
  - C–H amination 258, 259, 260, 262, 265–274
  - C–H bond catalytic oxidation
  - C–halogen bond-forming reactions 229–230
    - desaturation
      - – iron-based catalysts 41–42
      - – manganese-based catalysts 42–43
    - hydroxylation
      - – iron-based catalysts 38–39
      - – manganese-based catalysts 40–41
  - iron-based catalysts 34–37
  - manganese-based catalysts 37–38
  - desaturation
    - – iron-based catalysts 41–42
    - – manganese-based catalysts 42–43
  - hydroxylation
    - – iron-based catalysts 38–39
    - – manganese-based catalysts 40–41
  - chelating bidentate diphosphines 108–109
  - chirality transfer 195, 197, 198, 199, 203, 204, 206
  - chiral ligands 132, 136, 154, 239, 250, 251, 279, 282, *see also* bicyclo[2.2.2]octenes
    - imidate, application in enantioselective catalysis
      - – asymmetric diethylzinc addition 316
      - – asymmetric iridium (I)-catalyzed hydrogenations 318–320
      - – asymmetric palladium (0)-catalyzed allylic alkylations 316–318
      - – copper (I)-catalyzed asymmetric aziridination 315–316
    - privileged 309
  - chiral monodentate phosphorus ligands, in asymmetric hydrogenation 108–112
  - chiral oxazoline–alcohol ligands, one-step synthesis of 320–321
  - chiral spiro-2-alkoxy-imidazolidines synthesis 321–322
  - chiral spirocyclic borate ligands application, to catalytic enantioselective
    - Nozaki–Hiyama–Kishi reaction 303–305
  - chiral sulfenic acids 59
  - chloroperoxidase (CPO) 93, 94, 95, 96
  - chromium 279–281, 283, 284–285, 288, 299–303, 305
  - C–N bond formation 257–258
    - copper- and silver-catalyzed 260–265
    - historical background 258–260
    - rhodium-catalyzed 265–273
  - C–N-forming reactions 223–227
  - C–O bond-forming reactions 227–228
  - copper catalysis in arene and heteroarene functionalization 211
    - C–C bond-forming reactions
      - – via aryl-h addition to terminal alkynes 223
      - – via (hetero)aryl-H/Ar<sub>2</sub>I<sup>+</sup>X-coupling 217–219
      - – via (hetero)aryl-H/R-X coupling 212–216
    - C–halogen bond-forming reactions 229–230
    - C–N-forming reactions 223–227
    - C–O bond-forming reactions 227–228
  - copper catalyzed reactions 343–345
  - cross-coupling reactions 338, 339, 340, 341–342, 343
  - cycloaddition and related reactions 335–338

cycloisomerization 195–198, 196, 197,  
198, 200–202, 200, 201, 202, 204, 205,  
206

## d

decalin-derived sulfenic acid synthesis and  
reactivity 49  
dehydroamino acid derivative asymmetric  
hydrogenation 105  
– catalyst precursors 112–117  
– chiral monodentate phosphorus ligands in  
asymmetric hydrogenation 108–112  
– MAC adducts  
– – evolution and enantioselection origin  
124–126  
– – formation 121–123  
– mechanistic insights 117–121  
density functional theory (DFT) 167,  
169–170  
diamagnetic term 113  
Diels–Alder reaction 335  
dihydride mechanism 106, 107  
dioxxygen 6

## e

effective core potentials (ECPs) 174  
electron correlation 168  
electron-donating phosphine 118  
enantiopure sulfenic acid 58  
enantiopure sulfinyl dienes synthesis, with  
central and axial chirality 59  
epimerization 197, 198  
epoxidation 90, 93  
– alkene 30–31, 33–34, 96–98  
– by aqueous TBHP 91  
– COT 90  
– iron-based catalysts 27–30  
– manganese-based catalysts 30–34  
– of simple olefines 92

## f

free energy surface (FES) 175, 176  
full configuration interaction 169

## g

$\alpha$ -D-glucopyranosyl sulfenic acid 55  
 $\beta$ -D-glucopyranosyl sulfenic acid 55  
Gaussian type orbitals (GTO) 172  
gold catalysis 195, 196–206

## h

Hartree–Fock (HF) method 168  
heteroarenes  
– dimerization 219–220

– direct alkenylation of 215–216  
– direct (hetero)arylation of 212–215,  
217–218

heterogeneous catalysts 142–144

heteropolyacids (HPAs) 6

Hf/Zr peroxopolyoxometalates 13–16  
homogeneous catalysis modeling 167

– basis sets 172–174  
– density functional theory 169–170  
– electronic structure 177–178  
– – AIM method 187–190  
– – NBO method 178–187  
– molecular modeling 167–168  
– orbitals 170–172  
– reaction energies 175–177  
– solvation 174  
– wave function theory 168–169

homogeneous catalysts 144–147  
homogeneous hydrogenation and

hydrogenolysis reactions, with  
dehydroamino acid derivatives and  
bicyclo[2.2.2]oct-7-enes 136

– nanometal colloids-modified catalysts  
136–140

– nanooxide colloids-modified catalysts  
140–142

Horner–Wadsworth–Emmons reaction 331

hydrogen peroxide 7, 77, 78, 84, 85, 86–91

– biocatalytic oxidations with  
– – alcohols oxidation 98–99  
– – alkenes epoxidation 96–98  
– – enzymes and HOOH 92–94  
– – sulfoxidation 95–96  
– oxidation, with vacant and hybrid POMs  
10–12  
– oxidation with, by  
peroxopolyoxotungstates-dendrimers  
8–10

hydroxyallenes cyclization 196–203

## i

imidates

– chiral ligands application in enantioselective  
catalysis

– – asymmetric diethylzinc addition 316

– – asymmetric iridium (I)-catalyzed  
hydrogenations 318–320

– – asymmetric palladium (0)-catalyzed allylic  
alkylations 316–318

– – copper (I)-catalyzed asymmetric  
aziridination 315–316

– and copper (I) complex synthesis 313–315

– cyclic 311–312

– – novel synthetic applications 320–322

imidates (*contd.*)  
 – ligand synthesis 313  
 – synthesis 312–313  
 ionic liquids (ILs) 12, 77, 80, 94, 97  
 – lipase-driven Baeyer–Villiger menthone  
 oxidation in hydrogen-bond-donating  
 98  
 – lipase-driven oxidation in 97  
 iridium, *see* olefins, Ir-catalyzed hydrogenation  
 of minimally functionalized

**k**

ketones 295

**l**

layered-double hydroxides, as support for  
 Rh(TPPTS)<sub>3</sub> and Rh(*m*-TPPTC)<sub>3</sub>  
 homogeneous catalysts 144–147  
 linear combination of atomic orbitals (LCAO)  
 172  
 lipase-driven epoxidation of alkenes 97  
 lipox system 94  
 local density approximation (LDA) 170

**m**

macrobicyclic cyclophane, sulfenic function  
 embedded in 51  
 mechanistic studies 265, 269, 271  
 metal-based selective oxidations 78  
 – alkenes oxidation 89–92  
 – bromination reactions 78–85  
 – nitrogen-containing substrates oxidation  
 85  
 – sulfur-containing substrates oxidation  
 85–89  
 metal catalysis 78, 83  
 metal-catalyzed reactions 338  
 – Cu-catalyzed reactions 343–345  
 – miscellaneous 345–347  
 – Mizoroki–Heck reaction 340–341  
 – Sonogashira reaction 341–343  
 – Suzuki–Miyaura reaction 338–340  
 metallanitrene reaction 258  
 metal-TPA complexes 84  
 methyl Z-2-acetamidocinnamate (MAC)  
 adducts  
 – evolution and enantioselection origin  
 124–126  
 – formation 121–123  
 Mizoroki–Heck reaction 340–341  
 molecular orbitals (MOs) 172, 173, 177, 187  
 monodentate phosphorus ligands, in  
 asymmetric hydrogenation 108–112

MONOPHOS 111, 114, 115, 116, 120–121,  
 125  
 monophosphines 109, 115  
 MP2 method 169

**n**

nanometal colloids modified catalysts  
 136–140  
 nanooxide colloids-modified catalysts  
 140–142  
 nanoparticles 136, 138, 139, 143  
 naphthalene 1,2-dioxygenase (NDO) 34, 36  
 natural bond orbital (NBO) method 177  
 – departure from Lewis structure 180–183  
 – and transition metal complexes 183–187  
 – working of 178–180  
 natural localized molecular orbital (NLMO)  
 182  
 natural product synthesis 280, 281, 286,  
 303, 304  
 nitrenes 257–261, 264–269, 271–272  
 nitrones 85, 86  
 Nozaki–Hiyama–Kishi reaction development  
 279  
 – catalytic 279–280  
 – – applications in total synthesis 303–305  
 – – enantioselective 281–282  
 – chiral spirocyclic borate ligands application  
 to catalytic enantioselective 303–305  
 – oxazoline-containing ligands application in  
 catalytic enantioselective 286–299  
 – Salen-derived ligands application in  
 enantioselective 283–286  
 – tethered bis(8-quinolinato) chromium  
 complexes application in catalytic  
 enantioselective 299–303

**o**

olefins, Ir-catalyzed hydrogenation of  
 minimally functionalized 153–155, 162,  
 319  
 – phosphite–nitrogen ligand application  
 155–161  
 one-pot Wittig reaction 331  
 organocatalytic methods 333  
 – asymmetric aldol reactions 333–334  
 – cycloaddition and related reactions  
 335–338  
 organocuprates 233  
 – accepted mechanistic proposals 233–234  
 – kinetic and NMR studies 235–242  
 – – challenges 245  
 – – computational studies 242–243  
 – – nonlinear effects 243–245

- privileged copper(I) catalysis selective applications
- – allylic halides additions 250–252
- – conjugate addition 245–250
- oxazoline-alcohol ligands, one-step synthesis of 320–321
- oxazoline-containing ligands application, in catalytic enantioselective
  - Nozaki–Hiyama–Kishi reaction 286–299
- oxidation catalysts, *see* polyoxometalates (POMs)
- oxidative enzymes classification 93
- OXONE<sup>®</sup> 29, 34, 35, 41, 42
- oxygenases 92
- oxygen donor (OD) 77, 78

## p

- palladium-catalyzed allylic sulfinylation 67, 68, 69
- paramagnetic term 113
- peptides, solvent-free synthesis of 332
- peroxidases 93
- PhIO 42
- phosphite–nitrogen ligands, application of 155–161
- polarization 173
- polyanions 3–4, 5, 10, 13, 14,
- polyoxometalates (POMs) 3
  - homogeneous oxidations with 6–8
  - – aerobic oxidations with polyoxopalladates 16–17
  - – Hf/Zr peroxopolyoxometalates 13–16
  - – with hydrogen peroxide by peroxopolyoxotungstates-dendrimers 8–10
  - – with hydrogen peroxide with vacant and hybrid POMs 10–12
  - – TMSPs as oxygen-evolving catalysts 17–19
  - – with TMS-POMs 12–13
  - soluble metal oxides 3–6
- polyoxopalladates, aerobic oxidations with 16–17
- Pople sets 173
- potential energy surfaces 168, 175, 189, 190
- pseudodomino sulfenate generation/arylation process mechanism 72
- pseudodomino sulfinylation/Mizoroki–Heck process postulated mechanism 71
- pseudo-thiodisaccharides, via a glucosulfenic acid 60

## q

- quantum mechanical methods 167–170, 175

## r

- reaction energies 175–177
- rhodium-catalyzed C–N bond formation 265–273
- R–X=alkenyl bromides
  - arenes, direct alkenylation of 216
  - heteroarenes, direct alkenylation of 215–216
- R–X=BrCH<sub>2</sub>Ar
  - arenes, direct benzylation of 216
- R–X=(hetero)aryl halides
  - arenes, direct (hetero)arylation of 215
  - heteroarenes, direct (hetero)arylation of 212–215

## s

- Salen-derived ligands application, in enantioselective Nozaki–Hiyama–Kishi reaction 283–286
- salicylic acid 37
- Schrödinger equation 167–168, 169
- $\sigma$ -donation 187
- Slater type orbitals (STO) 172
- solid-state reactions 335, 336, 347
- solvation 174
- Sonogashira reaction 341–343
- spirocyclic borate ligands application, to catalytic enantioselective
  - Nozaki–Hiyama–Kishi reaction 303–305
- split-valence (SV) basis set 173
- Streptococcus lactis* 131
- Streptomyces niveus* 131
- Streptomyces spheroides* 131
- sulfenate anions
  - decomposition 63
  - first isolation of 64
  - formation from sulfenate silyl esters 64
  - generation of transient 65–73
  - strategies towards generation of 64
  - via addition–elimination 65
  - via alkaline heterocyclic disulfides hydrolysis 64
- sulfenic acids 47–48
  - in alliin analogs synthesis 60
  - $\alpha$ -D-glucopyranosyl 55
  - $\beta$ -D-glucopyranosyl 55
  - cation 50
  - cephalosporin-derived 52
  - chiral 59

sulfenic acids (*contd.*)

- formation by thionitrate function hydrolysis 52
- generation of transient 52–57, 56, 57, 58
- precursors from
  - 1,1-*bis*(phenylsulfonyl)ethylene 54
- reactivity, in sulfoxides and unsymmetrical disulfides preparation 57–62
- stable sulfenate anions synthesis 62–65
- synthesis of stable 48–52
- thiophene triptycene 50
- transient sulfenate anion generation leading to sulfoxides 65–73
- sulfoxidation 86, 87, 88, 89, 95
- biocatalytic 95–96
- sulfoxides
  - transient sulfenate anion generation leading to 65–73
  - and unsymmetrical disulfides preparation, sulfenic acid reactivity in 57–62
- sustainable catalytic oxidations, with peroxides 77–78
- biocatalytic oxidations with hydrogen peroxide
  - – biocatalytic alcohols oxidation 98–99
  - – biocatalytic alkenes epoxidation 96–98
  - – biocatalytic sulfoxidation 95–96
  - – enzymes and HOOH 92–94
  - metal-based selective oxidations 78
  - – alkenes oxidation 89–92
  - – bromination reactions 78–85
  - – nitrogen-containing substrates oxidation 85
  - – sulfur-containing substrates oxidation 85–89
- Suzuki–Miyaura reaction 338–340

**t**

- Tanaka reaction proposed mechanism 67
- tethered bis(8-quinolinato) chromium complexes application, in catalytic enantioselective Nozaki–Hiyama–Kishi reaction 299–303
- thioallenes cyclization 206
- thioglycoconjugates, from *bis*-sulfenic acids 61
- transition metal 257
  - catalysis 309, 313, 322
  - complexes 183–187
- transition metals substituted polyoxometalates (TMSPs) 3
  - as oxygen-evolving catalysts 17–19
- triazine-derived sulfenic acid 49
- triphenolamines (TPA) ligands 83, 84, 85, 86–87
- tripodal disulfides synthesis 63

**u**

- unsaturated mechanism 106–107

**v**

- valence double- $\zeta$  173
- vanadium-dependent bromoperoxidase (V-BrPO) enzymes 78–79

**w**

- wave function theory (WFT) 167, 168–169
- Wittig reaction, one pot 331