

# Subject Index

- Abyssomicin C. Nozaki-Hiyama-Kishi reaction, 312
- Acetals, Mukaiyama aldol reaction, 509
- Acetonitrile, Henry reaction, potassium phosphate-based procedure, 415
- Acetophenone, McMurry coupling, 275–276
- Acetylene
- Corey-Fuchs reaction, 396–401
  - Glaser coupling, organocopper reagents, 241–252
  - Sonogashira reaction, 109–110
- Acetylide formation, Castro-Stephens reaction, catalytic mechanism, 218–220
- Acetyl sulfones, Julia-Lythgoe olefination, vinyl sulfone conversion, 470
- Acid chloride, Arndt-Eistert homologation, 347–348
- Ac*-nitro(*p*-methoxy-phenyl)methane preparation, (*t*-butyl)Dimethylsilyl ester, 416
- Acylsilane, cross-benzoin condensation, 389
- Additives, Stille coupling, 140–142
- Alcohols
- Barton-McCombie deoxygenation, 616–617
  - Henry reaction, 411–412
  - Tsuji-Trost reaction and oxidation, 204–205
  - Wittig reaction variants, 599
- Aldehydes
- benzoin condensation
    - annulations, 386
    - basic principles, 380–381
    - cross-coupling reaction, 389
  - Corey-Fuchs reaction, 392–402
  - Henry reaction, 403–415
    - lithium salt and ketone, 416
    - silylnitronate, 416
  - Horner-Wadsworth-Emmons reaction, 421–423
  - Knoevenagel reaction, electrophilic scope, 487
  - McMurry coupling, 269–272
  - Mukaiyama aldol reaction, 504–505, 507–508
  - Sakurai allylation reaction, Lewis acid-carbonyl complex, 544–546
  - Tebbe methylenation, 324–327
- Aldo condensation, Henry reaction and, 403
- Aldol reaction
- Knoevenagel mechanism, 476–478
  - Mukaiyama aldol reaction
    - basic principles, 501
    - diastereoselective synthesis, 504–509
    - enantioselective variants, 512–517
    - historical perspective, 501–502
    - mechanism, 502–504
    - synthetic utility, 504–517
    - tandem reactions, 511–512
    - TMS compounds, 517–518
    - vinologous reaction, 509–511
  - Nicholas reaction modification, 288–289
- Aldonolactones, Tebbe methylenation, 330–331
- Aldosterone, Barton nitrite photolysis reaction, 633
- experimental compounds, 643–645
  - steroid core functionalization, 635–638
- Alkaline earth metals, McMurry coupling, 272
- Alkaloids, Arndt-Eistert homologation, 341
- Alkenes
- Julia-Kocienski olefination, 455–459
  - Julia-Lythgoe olefination, 451–459
  - McMurry coupling, 270–271

- Alkenes (*continued*)  
Negishi cross-coupling reaction, 83–86  
Peterson olefination, 526  
Wittig reaction, 587–589  
  variations, 592–603  
Wohl-Ziegler reaction, 664–668
- I-(1-Alkenyl)benzotriazoles, Peterson  
  olefination, 529–530
- Alkenyl chloride reagents, Kumada cross-  
  coupling reactions, 52–59
- Alkoxides, Morita-Baylis-Hillman  
  homologation, 357
- Alkoxy phosphonate, Wittig reaction, 594–595
- $\beta$ -Alkoxy substituent, Sakurai allylation reaction,  
  554
- Alkyl bromides, Negishi cross-coupling  
  reactions, 74–75
- Alkyl halides  
  Kumada cross-coupling reactions, 63–64  
  Stille coupling, 147–149  
  Fu's procedure, 157  
  Suzuki coupling reactions, unactivated  
  compounds, 173–174
- Alkynes  
  Castro-Stephens reaction, silylated alkynes,  
  230  
  Corey-Fuchs reaction, 397–401  
  Glaser coupling, organocopper reagents,  
  238–241  
  Negishi cross-coupling reaction, 83–86  
  Sonogashira reaction, 105–106  
  homocoupling, 109–110  
  nontraditional coupling partners, 128
- Alkynylboronates, Glaser coupling,  
  organocopper reagents, 241
- Alkynyltrialkylsilanes, Glaser coupling,  
  organocopper reagents, 240–241
- Allenes, Wittig reaction modification, 600–601
- Allocholchicine, Nicholas reaction, 292–293
- Allylic compounds  
  Tsuji-Trost reaction, hydrogenolysis, 205–206  
  Wohl-Ziegler reaction, 665–668
- Allylic halides, Castro-Stephens coupling,  
  229–230
- Allylsilanes, Sakurai allylation reaction,  
  538–539  
  nucleophilicity, 546
- Aluminum compounds, Tebbe methylenation  
  basic properties, 319–321  
  Petasis olefination, 321–327
- Alzheimer's therapy  
  Barton-McCombie deoxygenation, 626–629  
  Corey-Fuchs reaction, 399–400
- Amburicin, Julia-Kocienski/Julia-Lythgoc  
  olefination, 465–466
- Amides  
  Corey-Fuchs reaction, 398–399  
  Negishi cross-coupling reaction, 89  
  Tebbe methylenation, 329–331  
  Wohl-Ziegler reaction, 668–672
- Amine nucleophiles  
  Knoevenagel reaction  
  historical perspective, 473–475  
  mechanism, 476–478  
  tertiary amines, 482  
  Verley-Doebner modification, 478–481  
  Tsuji-Trost reaction, 199–201
- $\beta$ -Amino acid synthesis, Arndt-Eistert  
  homologation, 337–338
- Amino acids  
  Knoevenagel reaction, catalysis by, 482–483  
  Dakin-Prout modification, 496  
  Negishi cross-coupling reaction, 87–89
- $\beta$ -Amino alcohols, Henry reaction, 408–410
- Aminosulfoximine ligands, Mukaiyama aldol  
  reaction, enantioselectivity, 516–517
- Amphidinol 3, Nozaki-Hiyama-Kishi reaction,  
  310
- Amphidinolide B1, Sakurai allylation reaction,  
  560–561
- Amprénarvir, Henry reaction, 409–410
- (+)-Ancistrofuran, Barton-McCombie  
  deoxygenation, 627
- Ando procedure, Horner-Wadsworth-Emmons  
  reaction, synthetic procedures, 429
- Androstane series, Barton nitrite photolysis  
  reaction, 636–638
- Anhydrides  
  Arndt-Eistert homologation, 346–347  
  Tebbe methylenation, 331
- Anilides, asymmetric intramolecular Heck  
  reaction, 13–17
- Anion-exchange resins, Henry reaction, 404
- Anionic pathways  
  Heck reaction, 7–9  
  Hiyama cross-coupling reaction, 34–35
- Annulation  
  benzoin condensation, 386

- Stetter reaction, asymmetric annulation, 585
- Annulene, Glaser coupling, organocopper reagents, 246–252
- Antascomycin A, Nozaki-Hiyama-Kishi reaction, 310
- Antibacterial agents  
Morita-Bayless-Hillman reaction, 374–375  
Sandmeyer reaction, 653–654
- Antibiotic agents  
Barton-McCombie deoxygenation, 628  
Julia-Kocienski/Julia-Lythgoe olefination, 463–469  
Mukaiyama aldol reaction, 508–509
- Anti coordination, Sakurai allylation reaction, 544  
*syn-anti* isomerism, 547–551
- Antidiabetic compounds, Knoevenagel reaction, 493
- Anti-inflammatory drugs, Knoevenagel reaction, 494
- Anti-influenza agents  
Wittig reaction, 606–607  
Wohl-Ziegler reaction, 669
- Antithrombotic compounds, Morita-Bayless-Hillman reaction, 374
- Anti-tubercular drugs, Morita-Bayless-Hillman reaction, 373
- Anti-tumor agents, Horner-Wadsworth-Emmons reaction, 430–443
- Antiviral agents, Mukaiyama aldol reaction, 506–509
- Aqueous solvents  
Heck reactions, 25–26  
Sonogashira reaction, 127–128
- Arndt-Eistert homologation, carbon-chain homologations  
acid chloride homologation using  $\text{PhCO}_2\text{Ag}$ , 347–348  
 $\beta$ -amino acid synthesis, 337–338  
basic principles, 335  
diazo group transfer, 343–344  
 $\alpha,\beta$ -epoxy diazomethyl ketone rearrangement, 341–342  
historical perspective, 335–336  
mechanisms, 336–337  
mixed anhydride homologation using  $\text{CF}_3\text{CO}_2\text{Ag}$ , 346–347  
natural product synthesis, 339–341  
synthetic utility, 337–343  
trimethylsilyldiazomethane, 344–345  
Wolff rearrangement, 342–343  
ynolate anions, 345–346
- Aromatic aldehydes, Nozaki-Hiyama-Kishi reaction, 309
- Artemisinin, Sakurai allylation reaction, 570–571
- Aryl bromides  
Sandmeyer reaction, 651  
Suzuki reaction, 167–168
- Aryl chlorides  
Sonogashira reaction, 124  
Stille coupling, 145–147  
Suzuki coupling reactions, 169–170
- Aryl compounds  
aryl tosylates, Kumada cross-coupling reactions, 60  
Hiyama cross-coupling reaction, 36–37  
Knoevenagel reaction, 486  
Kumada cross-coupling reactions, 52–59  
Negishi cross-coupling reactions, 73
- Aryl halides  
Nozaki-Hiyama-Kishi reaction, 309  
Sonogashira reaction, 124
- Arylmagnesium reagents, Negishi cross-coupling reactions, 80
- 4-Arylpiperidines, Negishi cross-coupling reactions, 81
- Aryl sulfoxides, Julia-Lythgoe olefination, 452–453
- Aryl triflates, Suzuki reaction, 167–168
- Arylzinc chlorides and bromide-vinyl tellurides, Negishi cross-coupling reaction, 83
- Asmarine A, Morita-Bayless-Hillman reaction, 367–368
- Asymmetric allylic alkylation (AAA), Tsuji-Trost reaction, 188–189  
amine nucleophiles, 199–201  
carbon nucleophiles, 196–197  
metal catalysts, 206–208  
oxygen nucleophiles, 198–199  
sulfur nucleophiles, 201
- Asymmetric reactions  
BAL-catalyzed benzaldehyde dimerization, 388–389  
Heck reactions  
intermolecular reaction, 17  
intramolecular reaction, 13–17

- Asymmetric reactions (*continued*)  
Henry reaction, chiral copper catalyst, 415  
Kumada cross-coupling, 55–57  
Morita-Baylis-Hillman homologation, 359–361  
Mukaiyama aldol reaction  
  enantioselectivity, 514–517  
  merged 1,2- and 1,3-asymmetric induction, 504–509  
Nicholas reaction, 286–289  
Nozaki-Hiyama-Kishi reaction, chiral  
  oxazoline ligands, 305–307  
Sakurai allylation reaction  
  1,2-asymmetric induction, 551–553  
  1,3-asymmetric induction, 554  
  catalytic reactions, 555–559  
Tsuji-Trost reaction, allylic alkylation, 188–190  
Ullman coupling, 265–266  
Atorvastatin, Stetter reaction, 577–578  
1-(*Z*)-Atractylodimol, Negishi cross-coupling reaction, 83–84  
Atropisomers, Wohl-Ziegler reaction, 670  
Aurisides A and B  
  Mukaiyama aldol reaction, enantioselectivity, 515–517  
  Nozaki-Hiyama-Kishi reaction, 312  
Aza-benzoin condensation, 387–388, 390  
Azadiradione, Barton nitrite photolysis reaction, 638–639  
Aza-Henry reaction, variation and improvements, 413  
Aza Morita-Baylis-Hillman reaction  
  basic principles, 361–362  
  intermolecular reactions, 377  
Azapiracid-1, Nozaki-Hiyama-Kishi reaction, 312  
Azidosphingosine, Julia-Kocienski olefination, 456–459  
Azobisisobutyronitrile (AIBN)  
  Barton-McCombie deoxygenation, 614–616  
  (*R*)-baclofen homologues, 626  
  4,6-dimethoxy-1-(tetradec-13'-enyl)-1*H*-indole, 630  
  miscellaneous reductants, 623–625  
  phosphorous-based reductants, 622–623  
  Wohl-Ziegler reaction, 668–671  
  deoxygenation, 626  
(–)-Bafilomycin A<sub>1</sub>, Mukaiyama aldol reaction, 505–506  
Bafilomycin A<sub>1</sub>, Stille coupling, 154  
Balz-Schiemann reaction, 649–650  
Barton-McCombie deoxygenation  
  basic principles, 613  
  4,6-dimethoxy-1-(tetradec-13'-enyl)-1*H*-indole, 630  
  historical perspective, 613–614  
  mechanisms, 614–616  
  miscellaneous alternative reductants, 623–625  
  phosphorous-based reductants, 622–623  
  silicon-based reductants, 619–621  
  synthetic utility, 625–629  
  1,1'-thiocarbonyldiimidazole, 629–630  
  tin-based reductants, 618–619  
  variation and improvements, 616–618  
Barton nitrite photolysis reaction  
  basic principles, 632  
  flexible molecule functionalization, 642  
  historical perspective, 632–634  
  9-hydroxy-2,2,4,8-tetramethyl-octahydro-4,8-methano-azulen-1-one oxime, 645  
  mechanisms, 634  
  non-steroidal rigid system functionalization, 638–642  
  steroid core functionalizations, 635–638  
  synthetic utility, 634–642  
  variations and improvements, 642–644  
Baylis-Hillman reaction. *See* Morita-Baylis-Hillman reaction  
Benzaldehyde  
  Knoevenagel reaction, 474–478  
  Verley-Doebner modification, 478–481  
  NaCN-catalyzed dimerization, 388  
  Nozaki-Hiyama-Kishi reaction, 303  
Benzaldehyde lyase (BAL)  
  asymmetric benzaldehyde dimerization, 388–389  
  benzoin condensation, enantioselective dimerization, 383–385  
Benzalmalononitriles, Knoevenagel reaction, 491–495  
Benzofurans, Negishi cross-coupling reactions, 90  
Benzoin condensation  
  carbon-chain homologations

- annulations, 386  
aza-benzoin condensation, 387, 390  
BAL-catalyzed benzaldehyde dimerization, 388–389  
basic principles, 380–381  
cross-benzoin acylsilane-aldehyde coupling, 389  
cross-benzoin condensation, 383–385  
dimerization, 382–383  
enantioselective cross-benzoin condensation, 384–385  
enantioselective dimerization, 382–383  
historical perspective, 381  
mechanisms, 381–382  
NaCN-catalyzed benzaldehyde dimerization, 388  
synthetic utility, 382–387  
Stetter reaction, 575–576  
Benzoyl peroxide, Wohl-Ziegler reaction, 670–671  
Benzopyrans, Nicholas reaction, 294  
Benzoylformate decarboxylase (BED), benzoin condensation, enantioselective dimerization, 383–385  
 $\alpha$ -Benzyloxy substituents, Sakurai allylation reaction, 555  
1-(Benzyloxy)-4-iodopyrazole, Negishi cross-coupling reactions, 77  
*N*-(3-Benzyloxy-2-oxo-1-phenyl-propyl)-carbamic acid *tert*-butyl ester, benzoin condensation, 390  
1-(4-Benzylphenyl)ethanone, Suzuki coupling reaction, 181  
Bergman cyclization, Nozaki-Hiyama-Kishi reaction, 307  
Betaines, Wittig reaction, 591  
Biaryl compounds  
  enantioselective cross-benzoin condensation, 385  
  Ullman coupling reaction, 263–265  
Bicyclic guanidine base, Horner-Wadsworth-Emmons reaction, 419–421  
BINAP compounds  
  Heck reaction  
    asymmetric intermolecular reactions, 17  
    neutral pathways, 6–7  
  Mukaiyama aldol reaction, enantioselectivity, 516–517  
Binaphthyl (BINOL) ligands  
  Mukaiyama aldol reaction, enantioselectivity, 515–517  
  Sakurai allylation reaction, chiral promoters, 557  
(*R*)-BINOL, Kumada cross-coupling, asymmetric reactions, 57  
Bioconjugates, Sonogashira reaction, 121–122  
Biologically active molecules, Knoevenagel reaction, 491–495  
Biomimetic Stetter reaction, 578  
Biopolymers, Sonogashira reaction, 115–117  
Bipimatin J, Nozaki-Hiyama-Kishi reaction, 311  
Bipyridines, Negishi cross-coupling reactions, 97  
Bipyridyl ligands, Nozaki-Hiyama-Kishi reaction, 301–302  
(*R*)-2,2'-Bis(bromomethyl)-1,1'-binaphthyl, Wohl-Ziegler reaction, 672  
6,6-Bis-phenylsulfonyl-4-(*tert*-butyldimethylsilyloxymethyl)-1-(4-methoxy-benzyloxy)-hex-3-en-2-ol, Tsuji-Trost reaction, 209  
Bis(trifluoromethyl)phenyl (BTfP), Julia-Lythgoe olefination, 457–459  
Borane compounds, Barton-McCombie deoxygenation, 625  
Boron trifluoride promoter, Sakurai allylation reaction  
  basic properties, 538–539  
  example, 569  
  Lewis acid-carbonyl complex, 542–543  
Borrelidin, Nozaki-Hiyama-Kishi reaction, 312  
Breslow mechanism, Stetter reaction, 575–576  
Brevenal, Suzuki coupling reactions, 179–180  
Brevetoxins  
  Sakurai allylation reaction, 561–562  
  Wittig reaction, 605–606  
Briarellins F and H, Nozaki-Hiyama-Kishi reaction, 311  
Bromination  
  Sandmeyer reaction, 655  
  Wohl-Ziegler reaction, mechanisms, 662–668  
6-Bromo-4-ethyl-3-(1-fluoro-1-methylethyl)chromate, Nicholas reaction, 297  
*N*-Bromosuccinimide (NBS), Wohl-Ziegler reaction, 660–672  
Bronze, Ullmann coupling, 261  
[1,2]-Brook rearrangement, benzoin condensation, 384–385

- Bryostatín, Mukaiyama aldol reaction, 507
- Bulky ligands
- Sonogashira reaction, 129–130
  - Suzuki coupling reactions, 170
- tert*-Butyl(4,4-dibromobut-3-en-2-yl)dimethylsilane, Corey-Fuchs reaction, 401
- tert*-Butyldimethyl(pent-3-yn-2-yl)silane, Corey-Fuchs reaction, 401–402
- Cadinane-sesquiterpene veticadimol, tandem
- Knoevenagel-ene reaction, 488
- Cadiot-Chodkiewicz reaction, Castro-Stephens reaction and
- organocopper reagents, 221–223
  - related processes, 231
- Camptothecin, Negishi cross-coupling reactions, 94
- Cannizzaro reaction, Henry reaction and, 403
- Carbazole synthesis, Sonogashira reaction, 120–121
- Carbenes, Heck reactions, 23
- Carbocations, Nicholas reaction, 286–289
- Carbohydrates, Negishi cross-coupling reaction, 87
- Carbonates, Barton-McCombie deoxygenation, 615
- Carbon-carbon bond formation
- Heck reaction, 2–3
  - Mukaiyama aldol reaction, enantioselectivity, 514–517
  - Negishi cross-coupling reactions, 75–76
    - organozinc reagents, 89
  - Nicholas reaction, 289
  - Peterson olefination, 521–522
  - Sonogashira reaction, 100–102
  - Stille coupling, sigma carbon bonds, 144–145, 148–149, 152–156
  - Suzuki reaction, 163
    - mechanisms, 165–166
- Carbon-chain homologations
- Arndt-Eistert homologation
    - acid chloride homologation using  $\text{PhCO}_2\text{Ag}$ , 347–348
    - $\beta$ -amino acid synthesis, 337–338
    - basic principles, 335
    - diazo group transfer, 343–344
    - $\alpha,\beta$ -epoxy diazomethyl ketone rearrangement, 341–342
    - historical perspective, 335–336
    - mechanisms, 336–337
    - mixed anhydride homologation using  $\text{CF}_3\text{CO}_2\text{Ag}$ , 346–347
    - natural product synthesis, 339–341
    - synthetic utility, 337–343
    - trimethylsilyldiazomethane, 344–345
    - Wolff rearrangement, 342–343
    - ynolate anions, 345–346
- benzoin condensation
- annulations, 386
  - aza-benzoin condensation, 387–390
- BAL-catalyzed benzaldehyde dimerization, 388–389
- basic principles, 380–381
- cross-benzoin acylsilane-aldehyde coupling, 389
- cross-benzoin condensation, 383–385
- dimerization, 382–383
- enantioselective cross-benzoin condensation, 384–385
- enantioselective dimerization, 382–383
- historical perspective, 381
- mechanisms, 381–382
- $\text{NaCN}$ -catalyzed benzaldehyde dimerization, 388
- synthetic utility, 382–387
- Corey-Fuchs reaction
- description, 392
  - historical perspective, 392–393
  - mechanisms, 393–394
  - synthetic utility, 396–401
  - tert*-butyl(4,4-dibromobut-3-en-2-yl)dimethylsilane, 401
  - tert*-butyldimethyl(pent-3-yn-2-yl)silane, 401–402
  - variation and improvement, 394–396
- Henry reaction
- alcohols, 411–412
  - $\beta$ -amino alcohols, 408–410
  - asymmetry procedure, chiral copper catalyst, 415
  - aza-Henry reaction, 413
  - basic principles, 403–404
  - historical perspective, 404
  - $\alpha$ -hydroxycarboxylic acids, 412–413
  - $\alpha$ -hydroxyketones, 411
  - intramolecular reaction, 414
  - lithionitrate, aldehydes and ketones, 416

- mechanism, 404–405
  - nitroalkenes, 406–408
  - $\alpha$ -nitroketones, 410–411
  - nitronates condensation, 414
  - 6-nitro-7-trimethylsilyloxytridecane, 417
  - potassium phosphate-based acetone nitrile procedure, 415
  - retro-Henry reaction, 415
  - silylnitronate and aldehyde, 416–417
  - synthetic utility, 405–413
- Hornor-Wadsworth-Emmons reaction**
- basic principles, 419–421
  - historical perspective, 421
  - mechanism, 421–423
  - methyl 4-*O*-acetyl-3-methoxy-(*Z*)-cinnamate, 443–444
  - natural product synthesis, 429–443
  - Still-Gennari variation, 423
  - synthetic utility, 424–429
- Julia-Kocienski olefination**
- mechanism, 449–450
  - natural product synthesis, 459–469
  - synthetic utility, 450–459
- Julia-Lythgoe olefination**
- acetoxysulfone-vinyl sulfone conversion, 470
  - alkyl sulfone-aldehyde coupling, 469–470
  - basic principles, 446–447
  - historical perspective, 447–448
  - mechanism, 448–449
  - natural product synthesis, 459–469
  - synthetic utility, 450–459
  - vinyl sulfone reductive cleavage, 470–471
- Knoevenagel reaction**
- active methylene nucleophile, 484
  - amino acid catalysis, 482–483, 496
  - aryl/heteroaryl activating groups, 486
  - basic principles, 473
  - condensation promoters, 483–484
  - Cope modification, 482, 495–496
  - cynoacetic acid and esters, 485
  - Dakin-Frost modification, 496
  - diethyl 5 $\alpha$ -cholestan-3-ylidinemalonate, 496
  - 1,3-diketones, 486
  - electrophile scope, 487
  - ene reaction, 488
  - ethyl (1-ethylpropylidene)cynoacetate, 495–496
  - ethyl *n*-butylideneacetoacetate, 495
  - heterocycles, 486, 491
  - historical perspective, 473–476
  - $\beta$ -keto esters, 485
  - Lehnert modification, 483, 496
  - malonic acid, 484
  - malonic esters, 485
  - malononitrile, 485
  - mechanism, 476–478
  - natural products and bioactive molecules, 491–495
  - Nokami hydroxylative variant, 481–482
  - Ragoussis modification, 497
  - standard conditions, 482
  - stereochemistry, 487
  - synthetic utility, 484–495
  - tandem reactions, 487–488
    - Diels-Alder reaction, 488–489
    - electrocyclization, 489–490
    - Knoevenagel-Mislow-Evans, 490–491
  - Verley-Doebner modification, 478–481, 497
- Morita-Baylis-Hillman reaction**
- asymmetric reactions, 359–362
  - aza variant, 361–362
  - basic properties, 349
  - catalyst, 355–358
  - DABCO mediated intermolecular reaction, 375–376
  - high speed ball milling technique, 358–359
  - historical perspective, 349–350
  - intermolecular aza-MBH, 377
  - intramolecular reaction, 376–377
  - mechanism, 350–353
  - medicinal chemistry, 371–375
  - solvent effects, 353–355
  - synthetic utility, 362–375
  - titanium-mediated intermolecular reaction, 376
- Mukaiyama aldol reaction**
- basic principles, 501
  - diastereoselective synthesis, 504–509
  - enantioselective variants, 512–517
  - historical perspective, 501–502
  - mechanism, 502–504
  - synthetic utility, 504–517
  - tandem reactions, 511–512
  - TMS compounds, 517–518
  - vinologous reaction, 509–511

Carbon-chain homologations (*continued*)

## Peterson olefination

- basic principles, 520
- experimental compounds, 534–536
- historical perspective, 520–521
- mechanism, 521–522
- synthetic utility, 525–534
- variations and improvements, 523–525

## Sakurai allylation reaction

- 1,2-asymmetric induction, 551–553
- 1,3-asymmetric induction, 554
- asymmetric catalytic reactions, 555–559
- basic principles, 538–539
- BF<sub>3</sub> promoter, 569
- chiral silane chirality transfer, 554–555
- crotylsilanes, 567–568
- E/Z* isomerism, 547
- FeCl<sub>3</sub> promoter in MeNO<sub>2</sub>, 571–572
- historical perspective, 539–540
- mechanism, 540–546
  - aldehyde substituents, 545
  - Lewis acid-carbonyl complex, 542–545
  - silane substituents, 545–546
- SNCl<sub>4</sub> promoter, 569–570
- syn/anti* isomerism, 547–551
- synthetic utility, 560–567
- synthons, 559–560
- TiCl<sub>4</sub> promoter, 568–570
- ZnCl<sub>2</sub> promoter, 570–571

## Stetter reaction

- asymmetric intramolecular annulation, 585
- basic principles, 575
- biomimetic reactions, 578
- enantioselective reactions, 579–583
- historical perspective, 575
- intermolecular reactions, 576–580, 583–585
- intramolecular reactions, 580–582, 584
- mechanism, 575–576
- NaCN-catalyzed intermolecular reaction, 583–584
- Sila-Stetter reaction, 578–579, 584–585
- synthetic utility, 576–582
- thiazolidine-catalyzed intermolecular reaction, 584

## Wittig reaction

- basic principles, 587
- ethyl cyclohexylideneacetate, 609
- historical perspective, 587–588
- mechanism, 588–592

methylenecyclohexane, 608–609

synthetic utility, 603–608

variations, improvements, and modifications, 592–603

## Carbon nucleophiles, Tsuji-Trost reaction

- asymmetric allylic alkylation, 196–197
- “hard” nucleophiles, 195–196
- “soft” nucleophiles, 190–193

## Carbonylation

- Stille coupling, 137–138, 158
- Tsuji-Trost reaction, 202–203

## Carbonyl compounds

- Mukaiyama aldol reaction, 501–502
- Sakurai allylation reaction, 538–539
  - mechanism, 540–546
  - syn/anti* isomerism, 547–551
- Tebbe methylenation, 327–331
- Wittig reaction, 594

## Carboxylates, Tsuji-Trost reaction, asymmetric allylic alkylation, 198–199

## Caribenolide I, Morita-Bayless-Hillman reaction, 366

## Cascade cyclizations, Heck zipper reactions, 18

## Castro-Stephens reaction

- organocopper reagents
  - allylic halides, 229–230
  - aryl halide alkynylation, 224–225
  - basic principles, 212–214
  - catalytic mechanism and *in situ* acetylide formation, 218–220
- Catiot-Chodkiewicz reaction, 221–223, 231
- classical mechanism, 217–218
- copper-catalyzed Sonogashira, 229
- copper(I) acetylide preparation, 231–232
- copper nanoclusters - heterogeneous catalysis, 228–229
- heterocycle synthesis, 226–227, 233
- historical perspective, 214–216
- ligand effects, 220–221
- macrocycle synthesis, 225–226
- methyl 2-(2-(5-(methoxycarbonyl)benzofuran-2-yl)ethyl)benzofuran-5-carboxylate, 234
- 2-phenylfuro[3,2-*b*]pyridine, 233–234
- regioselectivity and stereoselectivity, 220
- Rosenmund-von Braun reaction, 223–224, 232
- silylated alkynes, 230
- in situ* modification, 234

- synthetic utility, 224–227
- palladium-free Sonogashira reaction, 128
- Sonogashira reaction, 102–103
- Catalytic reactions
  - Castro-Stephens reaction, acetylide formation, 218–220
  - Heck reaction, 3–12
  - Knoevenagel reaction, amino acids, 482–483
  - Morita-Baylis-Hillman homologation, 355–358
  - Sakurai allylation reaction, asymmetric reactions, 555–559
  - Stille coupling
    - alkyl halides, 147–149
    - aryl chloride case, 145–147
    - Suzuki coupling reactions, 168–169
- Catenanes, Glaser coupling, organocopper reagents, 249–252
- Cationic pathways, Heck reaction, 5–7
- Ceric ammonium nitrate (CAN), Nicholas reaction, 286–289
- Cerium chloride, Peterson olefination, 523–525
- Cesium fluoride, Peterson olefination, 523–525
- CF<sub>3</sub>CO<sub>2</sub>Ag, Arndt-Eistert homologation of mixed anhydrides, 346–347
- Chair-like transition state, Mukaiyama aldol reaction, 503–504
- Chalcogenide, Morita-Baylis-Hillman homologation, 358–359
- Chartelline A, Sandmeyer reaction, 651
- Chelation model, Sakurai allylation reaction, 552
- Chiral acyloxyborane (CAB) catalyst, Sakurai allylation reaction, 556
- Chiral binaphthalenes, Negishi cross-coupling reactions, 81–82
- Chiral copper catalysts, Henry reaction, 407–408
  - asymmetric reactions, 415
- Chiral ligands
  - Barton nitrite photolysis reaction and, 641
  - Wittig reaction variants, 599–603
- Chiral oxazoline ligands, Nozaki-Hiyama-Kishi reaction, 303–307
- Chiral salen ligands, Nozaki-Hiyama-Kishi reaction, 302–303
- Chiral silanes, Sakurai allylation reaction, chirality transfer, 554–555
- Chiral thiazolium precatalyst, benzoin condensation, enantioselective dimerization, 382–383
- Chlorination, Sandmeyer reaction, 655–656
- p*-Chlorobenzaldehyde, Morita-Baylis-Hillman homologation, 356–357
- Cholesterol derivatives, Barton nitrite photolysis reaction, 637–638
- Chroman-4-one, intramolecular Stetter reaction, 581
- Chromium catalysts, Nozaki-Hiyama-Kishi reaction, 300–301
- Ciganek-type reactions, Stetter reaction, 581–583
- Ciguatoxins, Nozaki-Hiyama-Kishi reaction, 310
- Cis-trans* isomerization, Negishi cross-coupling reactions, 72
- Claisen rearrangement
  - Arndt-Eistert homologation, diazo group transfer, 343–344
  - Knoevenagel reaction, 475
  - Sakurai allylation reaction, 562
  - Tebbe methylenation, 328–331
- Clavulone analogs, Sonogashira reaction, 113–114
- Cobalt
  - Kumada cross-coupling reactions, 64–66
  - Sandmeyer reaction, 649–650
- Collidine, Barton-McCombie deoxygenation, 624–625
- Combinatorial library synthesis, Sonogashira reaction, 113–114
- Complex fragment coupling, Sonogashira reaction, 111–114
- Concanamycin F, Mukaiyama aldol reaction, 506
- Condensation promoters, Knoevenagel reaction, 483–484
- Conformational analysis, Barton nitrite photolysis reaction, 632–633
- Conjugated systems
  - Heck reactions, 19
  - Hiyama cross-coupling reaction, additions, 40–41
  - Peterson olefination, 525
  - Tsuji-Trost reaction, diene formation, 203–204
- Cope modification, Knoevenagel reaction, 482
- Copper acetylide
  - Cadiot-Chodkiewicz reaction, 221–223
  - silylated alkynes, 230
  - Castro-Stephens reaction

- Copper acetylide (*continued*)  
classical mechanism, 217–218  
experimental preparations, 232–233  
historical perspective, 215–216  
*in situ* catalytic mechanism, 218–220
- Copper catalysts. *See also* Organocopper reagents  
Henry reaction, 407–408  
asymmetric reactions, 415
- Mukaiyama aldol reaction, enantioselectivity, 513–517
- Sandmeyer reaction, 649–650
- Sonogashira reaction  
basic properties, 100–102  
Castro-Stephens reaction and, 229  
high-activity ligands, 125–125  
historical perspective, 102–103  
mechanisms of, 104–106
- Stille coupling, 140–142  
vinylstannanes, 155–156
- Copper-free Sonogashira reaction  
bulky phosphine ligand, 129  
historical perspective, 103  
mechanism of, 106–107
- Copper(I) phenylacetylide  
Castro-Stephens reaction, 233  
Glaser coupling, basic principles, 236–237
- Corey-Chaykovsky reaction. Wittig reaction modification, 602
- Corey-Fuchs reaction, carbon-chain homologations  
description, 392  
historical perspective, 392–393  
mechanisms, 393–394  
synthetic utility, 396–401  
*tert*-butyl(4,4-dibromobut-3-en-2-yl)dimethylsilane, 401  
*tert*-butyldimethyl(pent-3-yn-2-yl)silane, 401–402  
variation and improvement, 394–396
- Corey's synthesis, Barton nitrite photolysis reaction, 638–639
- Cornforth model, Sakurai allylation reaction, 553
- Corticosterone acetate, Barton nitrite photolysis reaction, 635–636
- Cristatic acid, Tsuji-Frost reaction, 193
- (1)-Crocin, Peterson olefination, 528
- Cromakalim, Sandmeyer reaction, 654
- Cross-benzoin condensation, 384
- Cross-coupling reactions  
benzoin condensation  
acylsilane and aldehyde, 389  
basic principles, 380–381
- Castro-Stephens reaction  
allylic halides, 229–230  
classical mechanism, 217–218
- Hiyama cross-coupling, 33–45  
basic principles, 33  
conjugate additions, 40–41  
experimental compounds, 45  
heterocycle examples, 39–40  
historical perspective, 33–34  
improvements, 36–38  
mechanisms, 34–35  
natural product applications, 43–44  
organosiloxane preparations, 35–36  
organosilyl precursors, 38–39  
synthetic utility, 38–44  
tandem reactions, 41–42
- Kumada cross-coupling  
alkyl halides, 63–64  
aryl tosylates, 60  
asymmetric cross-coupling, 55–57  
basic principles, 47–48  
highly-active nickel-catalyzed procedure, 67  
historical perspective, 48–49  
Knochel-type Grignard reagents and triarylmagnesiates, 60–63  
mechanisms of, 49–52  
metallic catalysis, 64–66  
natural product synthesis, 58–59  
standard nickel-catalyzed procedure, 66–67  
synthetic utility, 52–59
- McMurry coupling, historical perspective, 268–272
- Negishi cross-coupling  
alkenes, alkynes, polyenes, enynes, 83–86  
amides and esters, 89  
amino acids, 87–89  
basic principles, 70  
bipyridine, 97  
carbohydrates, 87  
carbon-carbon bond constructions, 76–77  
catalytic improvements, 74–75  
enantioselectivity, 75–76  
five-membered heterocycles, 77–79  
furanoenone, 96  
historical background, 71

- mechanisms, 71–72
  - microwave irradiation, 73–74
  - natural products, 90–95
  - phosphine ligands, 72–73
  - six-membered rings, 79–82
  - synthetic utility, 77–96
- Sonogashira reaction
- alkyne homocoupling and acetylene reactivity, 109–110
  - aqueous solvent reactions, 127–128
  - basic principles, 100–102
  - bioconjugates, 121–122
  - bulky phosphine ligand, copper-free conditions, 129–130
  - complex fragment coupling, 111–114
  - copper co-catalyst, 104–106
  - copper-free mechanism, 106–107
  - cylindramide intermediate, 129
  - electronic and optical properties of compounds, 117–118
  - fatty acids and polyunsaturated systems, 114–115
  - heterocycle synthesis, 118–121
  - heterogeneous catalysts, 109
  - historical perspective, 102–103
  - ligand activity, 123–125
  - ligand-free catalysts, 108, 125–127
  - mechanisms, 107–108
  - metal catalysts, 128
  - non-traditional coupling partners, 128
  - polymers, 122–123
  - regioselectivity and stereoselectivity, 108
  - self-assembly subunits, dendrimers, and biopolymers, 115–117
  - synthetic utility, 110–123
- Suzuki reaction
- aryl chlorides, 169–170
  - basic principles and trends, 163
  - 1-(4-benzylphenyl)ethanone, 181
  - comparisons with other cross-coupling reactions, 163–165
  - enantioselective reactions, 174–176
  - heteroaromatic compounds, 170–171
  - highly active catalysts, 168–169
  - historical perspective, 165–166
  - mechanism, 166–168
  - 5-(2'-methylphenyl)-1*H*-indole, 180–181
  - organotrifluoroborate reagents, 171–173
  - synthetic utility, 176–180
  - unactivated alkyl halides and sulfonates, 173–174
- Ullmann coupling
- asymmetric copper coupling, 265–266
  - basic principles and historical perspective, 258
  - intramolecular palladium coupling, 266
  - mechanisms, 258–259
  - synthetic utility, 262–265
  - variations, improvements, or modifications, 259–261
- Crotylsilanes, Sakurai allylation reaction, 567–568
- Crotyltrimethoxysilane, Sakurai allylation reaction, 558–559
- CS gas, Knoevenagel reaction, 491–492
- Cyanation, Sandmeyer reaction, 656–657
- Cyanide complexes
- benzoin condensation, 381
  - modified cross-condensation, 384–385
  - Peterson olefination, 531–532
- Cyanoacetic acid and esters, Knoevenagel reaction, 485
- Cyclic compounds, Nicholas reaction, tandem reactions, 294–296
- Cyclin-dependent kinases (CDKs), Negishi cross-coupling reactions, 95
- Cyclitol derivatives, Peterson olefination, 532
- Cyclization, Nozaki-Hiyama-Kishi reaction, large-sized ring systems, 307
- Cycloalkanes, Nicholas reaction, 290–291
- Cyclohexadienes, Barton-McCombie deoxygenation, silicon-based reductants, 621
- Cyclopentadiene, asymmetric intramolecular Heck reaction, 14–17
- Cyclopenten-2-one, Morita-Baylis-Hillman homologation, 356–357
- Cyclopropanes, Nicholas reaction, 288–289
- Cyclopropyl carboxaldehyde, Knoevenagel reaction, 492
- Cyclopropylsulfonides, Julia-Lythgoe olefination, 454–459
- Cylindramide intermediate, Sonogashira reaction, 129
- DABCO (1,4-diazobicyclo-[2.2.2]octane)
- Castro-Stephens reaction, ligand effects, 221
  - Morita-Baylis-Hillman reaction

- DABCO (1,4-diazobicyclo-[2.2.2]octane)  
(*continued*)  
asymmetric reactions, 359–361  
development of, 350  
intermolecular reactions, 375–376  
mechanisms, 350–353  
solvent effects, 354–355
- Sonogashira reaction, ligand-free catalysts,  
125–127
- (+)-Dactylolide, Peterson olefination and Prins  
cyclization reaction, 532
- Dakin-Prout modification, Knoevenagel  
reaction, 496
- Deacetoxyalcyonin acetate, alcyonin, Nozaki-  
Hiyama-Kishi reaction, 312
- Decarboxylation, Knoevenagel reaction, Verley-  
Doebner modification, 481
- (*E*)-Dec-3-enoic acid, Knoevenagel reaction, 497
- [18]-Dehydrodesoxyepothilone B, Kumada  
cross-coupling reactions, 59
- Dendrimers, Sonogashira reaction, 115–117
- (–)-Dendrobine, Wittig reaction modification,  
601
- 12-Deoxofukujusonorone, Barton nitrite  
photolysis reaction, 635–636
- Deoxygenation reactions  
Barton-McCombie deoxygenation  
basic principles, 613  
4,6-dimethoxy-1-(tetradec-13'-enyl)-1*H*-  
indole, 630  
historical perspective, 613–614  
mechanisms, 614–616  
miscellaneous alternative reductants,  
623–625  
phosphorous-based reductants, 622–623  
silicon-based reductants, 619–621  
synthetic utility, 625–629  
1,1'-thiocarbonyldiimidazole, 629–630  
tin-based reductants, 618–619  
variation and improvements, 616–618  
McMurry coupling, 273–276
- Deprotonation, Peterson olefination, 522
- Deuterium, Barton-McCombie deoxygenation,  
miscellaneous reductants, 624–625
- Diacylenes, Glaser coupling, organocopper  
reagents, 242–252
- Dialkylphosphites, Barton-McCombie  
deoxygenation, 622–623  
*endo*, *endo*-2,5-Diaminonorbomane  
(DIANANE), Nozaki-Hiyama-Kishi  
reaction, 303
- 9,9'-Dianthryldiacetylene (Eglinton  
modification), Glaser coupling, 253
- Diarylcations  
Sakurai allylation reaction, Lewis acid-  
carbonyl complex, 545–546  
Wohl-Ziegler reaction, 667–668
- Diastereoselective synthesis  
Mukaiyama aldol reaction, 504–509  
vinylogous variant, 510–511  
Sakurai allylation reaction  
 $\beta$ -alkoxy substituent, 554  
*syn/anti* isomerism, 547–551
- 1,8-Diazabicycloundec-7-ene (DBU), Morita-  
Baylis-Hillman reaction, 355–356
- (2*S*,3*S*,4*S*)-3-Diazoacetyl-1-ethoxycarbonyl-4-  
isopropenyl-2-trisopropyl-  
silyloxymethylpyrrolidine, Arndt-Eistert  
homologation, 347
- Diazo group transfer  
Arndt-Eistert homologation, 343–344  
Sandmeyer reaction, 647  
variations, 649–650
- Diazomethane, Arndt-Eistert homologation,  
343–347
- Diazonium salts, Heck reactions, 27
- (1*S*,2*S*,5*R*,6*R*)-5,6-Dibenzoyloxy-cyclohex-3-ene-  
1,2-diol, Peterson olefination, 534–535
- (1*S*,4*S*,5*R*,6*R*)-5,6-Dibenzoyloxy-cyclohex-2-ene-  
1,4-diol, Peterson olefination, 535
- Dibromoalkene formation, Corey-Fuchs  
reaction, 394–396
- Dibromo ylide, Corey-Fuchs reaction, 393–394
- 1,4-Dicarbonyl compounds, Stetter reaction,  
577–578
- 2,4-Dichloropurine, Negishi cross-coupling  
reaction, 82
- Dichloroquinoline, Negishi cross-coupling  
reaction, 82
- Dictyostatin, Horner-Wadsworth-Emmons  
reaction, 432
- 1,3-Dicyclohexadienes, Peterson olefination, 534
- Dicyclohexylcarbodiimide (DCC), Henry  
reaction, 406–408
- Diels-Alder reaction  
Glaser coupling, organocopper reagents,  
244–252  
Peterson olefination, 525

- tandem Knoevenagel reaction, 488–489  
Tsuji-Trost reaction, carbon nucleophiles, 193  
Wittig reaction, 607
- Dienes, Julia-Lythgoe olefination, 456–459
- Dienones, Peterson olefination, 525
- Diethyl 5 $\alpha$ -cholestan-3-ylidinemalonate,  
Knoevenagel reaction, 496
- Diethylmalonate, Knoevenagel reaction, 475
- Dihydrobenzofuranone, intramolecular Stetter  
reaction, 581
- 5,7-Dihydro-dibenzo[a,c]cycloheptane-6,6-  
dicarboxylic acid diethyl ester, Ullman  
coupling, 266
- 1,22-Dihydroxyntiananes, Nozaki-Hiyama-Kishi  
reaction, 311
- 1,3-Diketones, Knoevenagel reaction, 486
- Dimerization  
BAI-catalyzed asymmetric benzaldehyde  
dimerization, 388–389  
benzoin condensation, 382–383  
NaCN-catalyzed benzaldehyde, 388
- 4,6-Dimethoxy-1-(10'-*N*-  
imidazolylthiocarbonyloxy)-tetradec-13'-  
enyl)-1*H*-indole, Barton-McCombie  
deoxygenation, 629–630
- 4,6-Dimethoxy-1-(tetradec-13'-enyl)-1*H*-indole,  
Barton-McCombie deoxygenation, 630
- Dimethylaminopyridine (DMAP), Morita-Baylis-  
Hillman homologation, 356
- (*R*)-2,2'-Dimethyl-1,1'-binaphthyl, Kumada  
cross-coupling reaction, 67
- 2,6-Dimethylbiphenyl, Hiyama cross-coupling  
reaction, 45
- Dimethylfuran (DMF), Castro-Stephens reaction,  
213–214
- N,N*-Dimethylglycine (DMG), Heck reactions,  
24–25
- (*E*)-3-(2,6-Dimethylphenyl)-3-methyl acrylic  
acid methyl ester, Heck reaction, 30
- (*n*-butyl)dimethylsilyl ester, *o**o*-nitro(*p*-  
methoxy-phenyl)methane preparation,  
416
- Dinitrile, Knoevenagel reaction, 491–492
- Dioxabicyclo-octene, Wohl-Ziegler reaction, 667
- Diphenylacetylene, Sonogashira reaction, 129
- 1,4-Diphenyl-2-(phenylsulfonyl)-1-butene,  
Julia-Lythgoe olefination, 470
- Diphenylphosphine, Wittig reaction variants,  
597–598
- 1,3-bis(Diphenylphosphino)propane (dppp)  
Heck reaction, neutral pathways, 6–7  
Kumada cross-coupling reactions, 53–59
- 1,4-Di-(2'-quinoly)-1,3-butadiyne (Cameron  
modification), Glaser coupling, 252–253
- (1)-Discodermolide, Nozaki-Hiyama-Kishi  
reaction, 312
- Discodermolide, Horner-Wadsworth-Emmons  
reaction, 434–437
- 2',4-Disubstituted-2,4'-bithiazoles, Negishi  
cross-coupling reactions, 91–92
- 1,1-Di-*t*-butyl peroxide (DTBP), Barton-  
McCombie deoxygenation, silicon-based  
reductants, 620–621
- 1,2-Dioxanthate, Barton-McCombie  
deoxygenation, 615–616
- Diyne, Negishi cross-coupling reaction, 86
- Dopamine-uptake inhibitors, Sandmeyer  
reaction, 653–654
- Drugs, Arnol-D, Arnol-E, Arnol-F homologation, 341
- Drug discovery analogues, Nozaki-Hiyama-  
Kishi reaction, 314
- Dynamic kinetic asymmetric transformation  
(DYKAT), Tsuji-Trost reaction  
asymmetric allylic alkylation, 190  
molybdenum-catalyzed reaction, 207
- Ebelactone A, Nozaki-Hiyama-Kishi reaction,  
312
- (-)-Efaroxan, Morita-Bayless-Hillman reaction,  
371–372
- Eglinton conditions, Glaser coupling,  
organocopper reagents, 240–241
- Eicosnoid 4, Nozaki-Hiyama-Kishi reaction, 311
- Electrocyclization, tandem Knoevenagel  
reaction, 489–490
- Electronic compounds, Sonogashira reaction,  
117–118
- Electrophiles  
Knoevenagel reaction, 487  
Wittig reaction, 596–603
- Enamides, Peterson olefination, 526–527
- Enantioselectivity  
benzoin condensation  
cross-benzoin reaction, 384–385  
dimerization, 382–383  
Mukaiyama aldol reaction, 512–517  
Sakurai allylation reaction, chiral promoters,  
556–559

- Enantioselectivity (*continued*)  
  Stetter reaction  
    intermolecular reactions, 579–580  
    intramolecular reactions, 581–583  
  Suzuki coupling reactions, 174–176
- Endocyclic intramolecular reactions, Nicholas reaction, 292–293
- Endothelin receptor antagonist, Barton nitrite photolysis reaction, 644
- Ene diyne antitumor agent, Nicholas reaction, 292–293
- Ene reactions  
  Mukaiyama aldol reaction, 503–504  
  tandem Knoevenagel reaction, 488
- Enolates, Wittig reaction, 604
- Enol silane, Mukaiyama aldol reaction, 507–509
- Enthalpies, Sakurai allylation reaction, Lewis acid-carbonyl complex, 543
- Enynes, Negishi cross-coupling reaction, 83–86
- Epothilones  
  Horner-Wadsworth-Emmons reaction, 439–443  
  Nozaki-Hiyama-Kishi reaction, 312
- Epoxydes, Mukaiyama aldol reaction, 512
- $\alpha,\beta$ -Epoxy diazomethyl ketone rearrangement, Arndt-Eistert homologation, 341–342
- Equilibrium constants, Sakurai allylation reaction, Lewis-Acid carbonyl complex, 542–543
- Erythrothreo* adducts, Wittig reaction, 589–590  
  variations, improvements or modifications, 592–603
- Esters  
  Negishi cross-coupling reaction, 89  
  Tebbe methylenation, Petasis olefination, 322–327
- Ethylacetoacetate, Knoevenagel reaction, 475–476
- Ethyl *n*-butylideneacetoacetate, Knoevenagel reaction, 495
- Ethyl cyclohexylideneacetate, Wittig reaction, 609
- Ethyl(diarylphosphono)acetates, Horner-Wadsworth-Emmons reaction, 420–421
- Ethyl (1-ethylpropylidene)cianoacetate, 495–496
- Ethyl (1-ethylpropylidene)cianoacetate, Knoevenagel reaction, 495–496
- Ethyl (1-methylpropylidene)cianoacetate, Knoevenagel reaction, 496
- (*R*)-Ethyl 2-(4-oxo-3,4-dihydro-2*H*-chromen-3-yl)acetate, Stetter reaction, 585
- N*-Ethylnylzine tosylamides, Negishi cross-coupling reaction, 85
- Evans synthesis, Mukaiyama aldol reaction, 504–509
- Exocyclic intramolecular reactions, Nicholas reaction, 293–294
- E/Z* isomerism, Sakurai allylation reaction, 547
- Farnesyl transferase, Arndt-Eistert homologation, 339–341
- Fatty acids, Sonogashira reaction, 114–115
- Felkin-Ahn model  
  Mukaiyama aldol reaction, 504–506  
  Peterson olefination, 526  
  Sakurai allylation reaction, 552
- Ferrocenylphosphine, Kumada cross-coupling, asymmetric reactions, 57
- Fischer carbene complex, Hiyama cross-coupling reaction, 38
- Five-membered heterocycles, Negishi cross-coupling reactions, 77–79
- “Flattened chair” conformation, steroid core, Barton nitrite photolysis reaction, 636–637
- Flexible molecules, Barton nitrite photolysis reaction, 642
- I*-Fluoro-*I*-haloalkenes, Negishi cross-coupling reaction, 84
- Fluoroquinolone antibiotics, Morita-Bayless-Hillman reaction, 372–373
- Fluorous systems, Heck reactions, 27
- $\alpha$ -Fluorovinylsulfones, Peterson olefination, 530
- Formates, Barton-McCombie deoxygenation, miscellaneous reductants, 624–625
- Formyl hydrogen bond, Sakurai allylation reaction, 544
- Forskolin compounds, Barton nitrite photolysis reaction, 641
- FR901512, Nozaki-Hiyama-Kishi reaction, 312
- Friedel-Crafts reaction  
  Mukaiyama aldol reaction, 503  
  Nicholas reaction, organometallic reagents, 285–286
- Furanoenyne, Negishi cross-coupling reactions, 96
- Furanosessquiterpene natural products, Barton-McCombie deoxygenation, 627

- (*Z*)-[4-(Furan-2-yl)buten-3-en-1-ynyl]trimethylsilane, Negishi cross-coupling reactions, 96
- Fu's protocol
- Barton-McCombie deoxygenation, tin-based reductants, 618–619
  - Heck reactions, 30
  - Hiyama cross-coupling reaction, 37–38
  - Stille coupling
    - alkyl halides, 157
    - sigma carbon bonds, 144–145, 148–149
- Gabosine precursor, Nozaki-Hiyama-Kishi reaction, 313
- Gelsmine, Knoevenagel reaction, 492
- GJI ring fragments, Sakurai allylation reaction, 561–562
- Glaser coupling, organocopper reagents
- basic principles, 236
  - 9,9'-dianthryldiacetylene (Eglinton modification), 253
  - 1,4-di-(2'-quinolyl)-1,3-butadiyne (Cameron modification), 252–253
  - 2,4-hexadiyne-1,6-diol, 252
  - historical perspective, 236
  - mechanism, 236–237
  - N,N'*-phenylbuta-1,3-diyne-1,4-tosylamide (Hay modification), 253
  - synthetic utility, 241–252
  - variations and improvements, 238–241
- C-Glycosides, Sakurai allylation reaction, 561–562
- Grignard reagents
- Kumada cross-coupling
    - asymmetric reactions, 56–57
    - basic principles, 47–48
    - Knochel-type reagents, 60–63
    - mechanisms of, 52–59
    - metal catalysis, 64–66
  - Suzuki reaction, 164–165
- Crubbs reagents, Tebbe methylation, 325–327
- Guanacastepene C, Knoevenagel reaction, 493
- Gymnoascolide A, Wohl-Ziegler reaction, 669
- Halichlorine, Montan-Bayless-Hillman reaction, 362
- Halides
- Sandmeyer reaction, 649–650
  - Sonogashira reaction, 128
  - Wohl-Ziegler reaction, 666–668
- (*Z*)-haloallylic alcohols, Nozaki-Hiyama-Kishi reaction, 308
- Halogenated alkenols, Nozaki-Hiyama-Kishi reaction, 308
- Halogenating agents, Wohl-Ziegler reaction, 671
- Hammett studies, Castro-Stephens reaction, classical mechanism, 218
- Hann-Lapworth mechanism, Knoevenagel reaction, 477–478
- Hantzsch's synthesis, Knoevenagel reaction, 473–474
- "Hard" nucleophiles, Tsuji-Trost reaction
- basic mechanism, 187–188
  - carbon nucleophiles, 195–196
- Heteroamals, Nozaki-Hiyama-Kishi reaction, 313
- Hay conditions, Glaser coupling, 238
- Heck reaction, palladium chemistry, 2–31
- alternative solvents, 25–27
  - anionic pathways, 7–9
  - aqueous media, 25–26
  - asymmetric intermolecular reaction, 17
  - asymmetric intramolecular reaction, 13–17
  - basic principles, 2
  - carbenes, 23
  - cationic vs. neutral pathways, 5–7
  - conjugated systems, 19
  - fluorous systems, 27
  - Fu's experimental conditions, 30
  - high-activity ligands, 20–23
  - historical perspective, 2–3
  - ionic liquids, 26–27
  - Jeffery's experimental conditions, 30–31
  - leaving groups, 27
  - ligand-free catalysts, 11–12, 23–25
  - mechanisms, 3–12
  - metal catalysts, 28
  - palladacycles, 22–23
  - phosphines, 21–22
  - polymers, 20
  - reductive reactions, 28–29
  - regioselectivity and stereoselectivity, 9–10
  - supercritical fluids, 27
  - supported catalysts, 23–25
  - synthetic utility, 12–20
  - zipper reactions, 18

- Helicobacter pylori* antibiotics, Barton-McCombie deoxygenation, 628
- (-)-Hemioxazole, Mukaiyama aldol reaction, 507–508
- Hemioxazole A, Julia-Kocienski/Julia-Lythgoe olefination, 466–467
- Henry reaction
- carbon-chain homologations
  - alcohols, 411–412
  - $\beta$ -amino alcohols, 408–410
  - asymmetry procedure, chiral copper catalyst, 415
  - aza-Henry reaction, 413
  - basic principles, 403–404
  - historical perspective, 404
  - $\alpha$ -hydroxycarboxylic acids, 412–413
  - $\alpha$ -hydroxyketones, 411
  - intramolecular reaction, 414
  - lithionitrate, aldehydes and ketones, 416
  - mechanism, 404–405
  - nitroalkenes, 406–408
  - $\alpha$ -nitroketones, 410–411
  - nitronates condensation, 414
  - potassium phosphate-based acetonitrile procedure, 415
  - retro-Henry reaction, 415
  - silylnitronate and aldehyde, 416–417
  - synthetic utility, 405–413
  - 6-nitro-7-trimethylsilyloxytridecane, 417
- (*E*)-(+)-Hept-1-enyl)naphthalene, Hiyama cross-coupling reaction, 45
- (+)-Herbarumin I, Nozaki-Hiyama-Kishi reaction, 313
- Herboxidiene, Julia-Kocienski/Julia-Lythgoe olefination, 468–469
- Herrmann's catalyst, Heck reactions, palladacycles, 22–23
- Heteroaromatic compounds, Suzuki coupling reactions, 170–171
- Heteroaryl activating groups, Knoevenagel reaction, 486
- Heteroatomic nucleophiles, Nicholas reaction, 287–289
- intermolecular reactions, 291
- Heterocouplings
- Glaser coupling, organocopper reagents, 244–252
  - McMurry coupling, 269–272
- Heterocyclic chemistry
- Castro-Stephens reaction, 233–234
  - Hiyama cross-coupling reaction, 39–40
  - Knoevenagel reaction, 486, 491
  - Negishi cross-coupling reactions, five-membered heterocycles, 77–79
  - Sandmeyer reaction, 653–654
  - Sonogashira reaction, 118–121
  - Wittig reaction, 607–608
- Heterogeneous catalysis
- Sonogashira reaction, 109
  - Suzuki coupling reactions, 168–169
- Hexacarbonyl( $\mu$ - $(\eta^4$ -[2,4-dimethyl-2-(prop-2-yn-1-yl)-8-oxabicyclo[3.2.1]octan-3-one]))dicobalt, Nicholas reaction, 296–297
- 2,4-Hexadiyne-1,6-diol, Glaser coupling, 252
- Hexylbenzene, Kumada cross-coupling reaction, 67
- Highest occupied molecular orbitals (HOMOs), Tebbe methylenation, 320–321
- High speed ball milling (HSBM) technique, Morita-Baylis-Hillman homologation, 358–359
- Hikizimycin, Nozaki-Hiyama-Kishi reaction, 310
- Hirsutic acid C, intramolecular Stetter reaction, 580–581
- HIV inhibitors, Horner-Wadsworth-Emmons reaction, 424–429
- Hiyama cross-coupling reaction, palladium chemistry, 33–45
- basic principles, 33
  - conjugate additions, 40–41
  - experimental compounds, 45
  - heterocycle examples, 39–40
  - historical perspective, 33–34
  - improvements, 36–38
  - mechanisms, 34–35
  - natural product applications, 43–44
  - organosiloxane preparations, 35–36
  - organosilyl precursors, 38–39
  - synthetic utility, 38–44
  - tandem reactions, 41–42
- Hofmann-Löffler-Freytag reaction, Barton nitrite photolysis reaction and, 640–641
- (*R*)-(-)-Homocentric acid- $\gamma$ -lactone, Arndt-Eistert homologation, 341
- Homocoupling reactions
- alkynes, Sonogashira reaction, 109–110

- Glaser coupling, organocopper reagents, 239–241
- Ullman coupling, 264–265
- Homogeneous catalysts, Suzuki coupling reactions, 168
- Hopf's synthesis, McMurry coupling, 270–271
- Horner-Wadsworth-Emmons reaction
- carbon-chain homologations
  - basic principles, 419–421
  - historical perspective, 421
  - mechanism, 421–423
  - methyl 4-*O*-acetyl-3-methoxy-(*Z*)-cinnamate, 443–444
  - natural product synthesis, 429–443
  - Still-Gennari variation, 423
  - synthetic utility, 424–429
- Peterson olefination, 520–521
- Wittig reaction variations, 592–603, 604–605
- $\beta$ -Hydride elimination, Heck reaction, regioselectivity and stereoselectivity, 9–10
- Hydrogenolysis, Tsuji-Trost reaction, allylic compounds, 205–206
- (*L*)-3-Hydroxybakuchiol, Peterson olefination, 531
- $\alpha$ -Hydroxycarboxylic acids, Henry reaction, 412–413
- 2-Hydroxy-1,2-diphenylethan-1-one, benzoin condensation, 388
- (*R*)-2-Hydroxy-1,2-diphenylethan-1-one, benzoin condensation, 389
- $\alpha$ -Hydroxyketones, Henry reaction, 411
- Hydroxylation, Sandmeyer reaction, 657
- $\beta$ -Hydroxysilanes, Peterson olefination, 520–528
- 19-Hydroxytaxol, McMurry coupling, 278–279
- 9-Hydroxy-2,2,4,8-tetramethyl-octahydro-4,8-methano-azulen-1-one oxime, Barton nitrite photolysis reaction, 645
- Hypophosphorous acid, Barton-McCombie deoxygenation, 622–623
- Imidazomethyl phosphonates, Horner-Wadsworth-Emmons reaction, 425–429
- Immunosuppressive compounds, Mukaiyama aldol reaction, 506
- Indium complexes, Mukaiyama aldol reaction, enantioselectivity, 514–517
- Indole compounds
- Barton-McCombie deoxygenation, 628
  - 4,6-dimethoxy-1-(10'-(*N*-imidazolylthiocarbonyloxy)-tetradec-13'-enyl)-1*H*-indole, 629–630
  - 4,6-dimethoxy-1-(tetradec-13'-enyl)-1*H*-indole, 630
  - McMurry coupling, 281
  - Sandmeyer reaction, 654
- Indolizomycin, Julia-Kocienski Julia-Lythgoe olefination, 463
- Ingenol antitumor agent, Nicholas reaction, 292–293
- Initiators, Wohl-Ziegler reaction, 670–671
- Intermolecular reactions
- Horner-Wadsworth-Emmons reaction, 425–429
  - Morita-Bayless-Hillman reaction, 375–377
  - Nicholas reaction, 290–291
  - Sakurai allylation reaction, *syn/anti* isomerism, 550–551
  - Stetter reaction, 576–580, 583–585
  - biomimetic reactions, 578
  - enantioselectivity, 579–580
  - NaCN-catalyzed reaction, 583–584
  - Sifa-Stetter variant, 578–579, 584–585
  - thiazolylidene-catalyzed reaction, 584
- Intramolecular reactions
- Heck reaction, 13–17
  - Henry reaction, 414
  - Hiyama cross-coupling reaction, 43–44
  - Horner-Wadsworth-Emmons reaction, 425–429
  - Morita-Baylis-Hillman homologation, 376–377
  - Nicholas reaction
    - endocyclic compounds, 292–293
    - exocyclic reactions, 293–294  - Sakurai allylation reaction, *syn/anti* isomerism, 551
  - Stetter reaction, 580–583
  - asymmetric annulation, 585
  - Suzuki coupling reactions, 178–179
  - Tsuji-Trost reaction, allylation, carbon nucleophiles, 192–193
  - Ullman coupling, 266
  - Wittig reactions, 604
- Iodides, Negishi cross-coupling reaction, 85
- Iodination, Sandmeyer reaction, 657
- 5-Iodomidazole, Negishi cross-coupling reactions, 78

- Ionic liquids  
  Heck reactions, 26–27  
  Morita-Baylis-Hillman reaction, 355
- Iridium, Tsuji-Frost reaction, asymmetric allylic alkylation, 206–208
- Iron complexes  
  Kumada cross-coupling reactions, 64–66  
  Sakurai allylation reaction, FeCl<sub>3</sub>, promoter, 571–572  
  Sandmeyer reaction, 649–650
- Isocoumarin, Sonogashira reaction, 120
- Isomerization  
  Knoevenagel reaction, Verley-Doebner modification, 479–481  
  Sakurai allylation reaction  
    *E,Z* isomerism, 547  
    *syn/anti* isomerism, 547–551
- Jatrophone compound, Stille-Hegedus synthesis, 153
- Jeffery's conditions, Heck reactions, 19, 30–31  
  ligand-free and supported catalysts, 23–25
- Jerangolid D, Sakurai allylation reaction, 563–564
- Julia-Kocienski olefination, carbon-chain homologations  
  mechanism, 449–450  
  natural product synthesis, 459–469  
  synthetic utility, 450–459
- Julia-Lythgoe olefination, carbon-chain homologations  
  acetoxysulfone-vinyl sulfone conversion, 470  
  alkyl sulfone-aldehyde coupling, 469–470  
  basic principles, 446–447  
  historical perspective, 447–448  
  mechanism, 448–449  
  natural product synthesis, 459–469  
  synthetic utility, 450–459  
  vinyl sulfone reductive cleavage, 470–471
- (-)-Kainic acid, Arndt-Eistert homologation, 339
- Keck synthesis  
  Mukaiyama aldol reaction, 506  
  Sakurai allylation reaction, 567
- $\beta$ -Keto esters, Knoevenagel reaction, 485
- Keto esters, McMurry coupling, 277–278
- Ketones  
  Arndt-Eistert homologation, 339–341  
     $\alpha,\beta$ -epoxy diazomethyl ketone  
      rearrangement, 341–342  
  benzoin condensation, 380–381  
  Henry reaction, 416  
  Horner-Wadsworth-Emmons reaction, 425–429  
  Julia-Lythgoe olefination, 451–459  
  Knoevenagel reaction  
    electrophilic scope, 487  
    Lehnert modification, 483  
  McMurry coupling, 269–272  
  Negishi cross-coupling reaction, 85  
  Sakurai allylation reaction, *syn anti* isomerism, 548–551  
  Tebbe methylenation, 324–327  
  Wittig reaction modification, 597–603
- Knochel-type Grignard reagents, Kumada cross-coupling, 60–63
- Knoevenagel reaction, carbon-chain homologations  
  active methylene nucleophile, 484  
  amino acid catalysis, 482–483, 496  
  aryl/heteroaryl activating groups, 486  
  basic principles, 473  
  condensation promoters, 483–484  
  Cope modification, 482, 495–496  
  cyanoacetic acid and esters, 485  
  Dakin-Prout modification, 496  
  diethyl 5 $\alpha$ -cholestan-3-ylidinemalonate, 496  
  1,3-diketones, 486  
  electrophile scope, 487  
  ene reaction, 488  
  ethyl (1-ethylpyrrolidine)cyanoacetate, 495–496  
  ethyl *n*-butylideneacetoacetate, 495  
  heterocycles, 486, 491  
  historical perspective, 473–476  
   $\beta$ -keto esters, 485  
  Lehnert modification, 483, 496  
  malonic acid, 484  
  malonic esters, 485  
  malononitrile, 485  
  mechanism, 476–478  
  natural products and bioactive molecules, 491–495  
  Nokami hydroxylative variant, 481–482  
  Ragoussis modification, 497  
  standard conditions, 482  
  stereochemistry, 487  
  synthetic utility, 484–495

- tandem reactions, 487–488  
  Diels-Alder reaction, 488–489  
  electrocyclization, 489–490  
  Knoevenagel-Mislow-Evans, 490–491  
  Verley-Duebner modification, 478–481, 497
- Knots, Gilser coupling, organocopper reagents, 249–252
- Kumada cross-coupling reactions, palladium chemistry  
  alkyl halides, 63–64  
  aryl tosylates, 60  
  asymmetric cross-coupling, 55–57  
  basic principles, 47–48  
  highly-active nickel-catalyzed procedure, 67  
  historical perspective, 48–49  
  Knochel-type Grignard reagents and triarylmagnesiates, 60–63  
  mechanisms of, 49–52  
  metallic catalysts, 64–66  
  natural product synthesis, 58–59  
  Negishi cross-coupling reactions vs., 79  
  standard nickel-catalyzed procedure, 66–67  
  synthetic utility, 52–59
- Lactonamyacin, Negishi cross-coupling reactions, 93
- $\beta$ -Lactones, Mukaiyama aldol reaction, 511–512
- Lanostane derivatives, Barton nitrite photolysis reaction, 637–638, 642–643
- Lanthanum-(*R*)-binaphthol complex, Henry reaction, 408–410
- Lapworth mechanism, benzoin condensation, 381–382
- Large scale Stille coupling, procedures for, 159
- Laulimalide analogues  
  Horner-Wadsworth-Emmons reaction, 438–440  
  Nozaki-Hiyama-Kishi reaction, 314  
  Sakurai allylation reaction, 566–567
- (+)-Laurencin, Tebbe methylenation, 329–331
- Leaving groups, Heck reactions, 27
- Lehnert modification, Knoevenagel reaction, 483
- diethyl *Sac*-cholestan-3-ylidinemalonate, 496
- Leucaseandrolide  
  Horner-Wadsworth-Emmons reaction, 440  
  Mukaiyama aldol reaction, 509
- Lewis acid-mediated reactions, Sakurai allylation reaction, 538–539  
  mechanism, 540–546
- Ligand effects  
  Castro-Stephens reaction, 220–221  
  Heck reactions, 20–21  
  Hiyama cross-coupling reaction, 37–38  
  Kumada cross-coupling, asymmetric reactions, 55–57  
  Sonogashira reaction, 101–102  
  high-activity ligands, 123–125  
  mechanisms of, 195–196  
  Stille coupling, 139–140  
  Suzuki coupling reactions, 169–170
- Ligand-free catalysts  
  Heck reaction  
    basic mechanisms, 11–12  
    supported catalysts, 23–25  
  Sonogashira reaction, 108, 125–127
- Lithionitrate, Henry reaction, 416
- Lithium salts, Wittig reaction, 590, 596–603
- Lowest unoccupied molecular orbital (LUMO), Sakurai allylation reaction, Lewis acid-carbonyl complex, 544–546
- Macrolactins, Julia Kocienski/Julia-Lythgoe olefination, 460–461
- Macrolides  
  Horner-Wadsworth-Emmons reaction, 431–443  
  Mukaiyama aldol reaction, 507  
  enantioselectivity, 514–517  
  vinylogous variant, 509–511
- Magnesium compounds  
  Corey-Fuchs reaction, 395–396  
  Wittig reaction, 597
- Magnesium-halogen exchange, Kumada cross-coupling reactions, 61–63
- Malonic acid, Knoevenagel reaction, 484
- Malonic esters, Knoevenagel reaction, 485
- Malononitrile, Knoevenagel reaction, 485
- Manganese catalysts  
  Nozaki-Hiyama-Kishi reaction, 304–307  
  Stille coupling, 142
- Manglicols, Nozaki-Hiyama-Kishi reaction, 310
- Mannich addition products, aza-benzoin condensation, 387–388
- (+)-Massarinolin, Nozaki-Hiyama-Kishi reaction, 313
- McMurry coupling, organometallic reagents  
  basic principles, 268  
  historical perspective, 268–272

- McMurry coupling, organometallic reagents  
(*continued*)  
indole, 281  
mechanism, 273–276  
receptor, 281–282  
synthetic utility, 278–281  
variations, improvements, modifications,  
276–278
- MDL compound, Knoevenagel reaction,  
493–494
- Medicinal chemistry  
Morita-Bayless-Hillman reaction, 371–375  
Sandmeyer reaction, 653–654
- Meerwein-Ponndorf-Verley reduction, Peterson  
olefination, 525
- Meerwein reaction, 650
- Merged 1,2- and 1,3-asymmetric induction,  
Mukaiyama aldol reaction, 504–509
- Metal catalysts  
Heck reactions, 28  
Henry reaction,  $\beta$ -amino alcohols, 408–410  
Kunada cross-coupling reactions, 64–66  
Sonogashira reaction, 126–129  
Stille coupling, 141–142  
Tsuji-Frost reaction, 206–208
- (2*S*,3*E*,7*E*,11*S*)-13-Methoxy-2-  
(methoxymethoxy)-4,8,11-trimethyl-15-  
methylenebicyclo[9.3.1]pentadeca-  
1(14),3,7,13-tetraene, Peterson  
olefination, 535–536
- Methyl 4-*O*-acetyl-3-methoxy-(*Z*)-cinnamate,  
Horner-Wadsworth-Emmons reaction,  
443–444
- Methyl 6,6'-dimethyl-2,2'-bipyridine-4-  
carboxylate, Negishi cross-coupling  
reactions, 97
- Methylation reactions, Peterson olefination,  
523–525
- Methylenecyclohexane, Wittig reaction, 608–609
- Methylene nucleophiles, Knoevenagel reaction,  
484
- Methyl (2*S*,3*S*,4*S*)-1-Ethoxycarbonyl-4-  
isopropenyl-2-triisopropylsilyl-  
oxymethyl-pyrrolidin-3-ylacetate, Arndt-  
Eistert homologation, 347–348
- Methyl ketones, Mukaiyama aldol reaction,  
517–518
- Methyl 2-(2-(5-(methoxycarbonyl)benzofuran-2-  
yl)ethyl)benzofuran-5-carboxylate,  
Castro-Stephens reaction, 234
- 2-Methyl-7-phenyl-2,4-heptadiene,  
Julia-Lythgoe olefination, 470–471
- 5-(2'-Methylphenyl)-1*H*-indole, Suzuki coupling  
reaction, 180
- 3-Methyl-1-phenyl-2-(triethylsilyloxy)butan-1-  
one, benzoin condensation, 389
- $\alpha$ -Methyl substituent, Sakurai allylation reaction,  
551–553
- Methyl *tert*-butyl ether (MTBE), Stille coupling,  
148–149
- Methyl vinyl ketone (MVK), Morita-Baylis-  
Hillman reaction, 350–353
- (+)-Methynolide, Nozaki-Hiyama-Kishi reaction,  
313
- Michael addition and elimination  
Henry reaction,  $\alpha$ -nitroketones, 410–411  
Knoevenagel reaction, 474–475  
Morita-Baylis-Hillman reaction, 351–353  
Wittig reaction, 603–604
- Michaelis-Arbusov reaction, Horner-Wadsworth-  
Emmons reaction, 424–429
- Microwave irradiation  
McMurry coupling, 272  
Negishi cross-coupling reactions, 73–74  
Stille coupling, toxicity reduction, 150–151  
Ullman coupling, 264–265  
Wittig reaction variants, 598
- Mislow-Evans [2,3]sigmatropic rearrangement,  
Nokami hydroxylative Knoevenagel  
reaction, 481–482
- Moenocinol, Julia-Kocienski/Julia-Lythgoe  
olefination, 461–462
- Molybdenum, Tsuji-Frost reaction, 206–208
- Monofluoromethylenephosphonates, Peterson  
olefination, 530
- Morita-Baylis-Hillman reaction, carbon-chain  
homologations  
asymmetric reactions, 359–362  
aza variant, 361–362  
basic properties, 349  
catalyst, 355–358  
DABCO mediated intermolecular reaction,  
375–376  
high speed ball milling technique, 358–359  
historical perspective, 349–350  
intermolecular aza-MBH, 377  
intramolecular reaction, 376–377  
mechanism, 350–353

- medicinal chemistry, 371–375
  - solvent effects, 353–355
  - synthetic utility, 362–375
  - titanium-mediated intermolecular reaction, 376
- Mosin B, Nozaki-Hiyama-Kishi reaction, 313
- Mukaiyama aldol reaction
- basic principles, 501
  - diastereoselective synthesis, 504–509
  - enantioselective variants, 512–517
  - historical perspective, 501–502
  - mechanism, 502–504
  - synthetic utility, 504–517
  - tandem reactions, 511–512
  - TMS compounds, 517–518
  - vinologous reaction, 509–511
- NaCN-catalyzed dimerization
- benzaldehyde, 388
  - intermolecular Stetter reaction, 583–584
- (–)-Nakadomarin A, Barton-McCombie deoxygenation, 628–629
- Nanostructures, Sonogashira reaction, 116–117
- Naphthyl-naphthyl Negishi cross-coupling reaction, 81
- Narbonolide, Nozaki-Hiyama-Kishi reaction, 311
- Natural products
- Arndt-Eistert homologation, 339–341
  - Barton-McCombie deoxygenation, 626–629
  - Barton nitrite photolysis reaction, 634–642
  - Hiyama cross-coupling reaction, 43–44
  - Homer-Wadsworth-Emmons reaction, 429–443
  - Hörner-Wadsworth-Emmons reaction, 429–443
  - Julia-Lythgoe olefination, 459–469
  - Knoevenagel reaction, 491–495
  - Kumada cross-coupling reactions, 58–59
  - Morita-Bayless-Hillman reaction, 362–375
  - Mukaiyama aldol reaction, diastereoselective synthesis, 504–509
  - Negishi cross-coupling reactions, 90–96
  - Nozaki-Hiyama-Kishi reaction, 309–314
  - Sandmeyer reaction, 650–653
  - Sonogashira reaction, 112–114
  - Suzuki coupling reactions, 176–177
  - Tsuji-Trost reaction, carbon nucleophiles, 193
- (–) and (+)-Negillamine A<sub>2</sub>, Nozaki-Hiyama-Kishi reaction, 313
- Negishi cross-coupling reactions, palladium chemistry
- alkenes, alkynes, polyenes, enynes, 83–86
  - amides and esters, 89
  - amino acids, 87–89
  - basic principles, 70
  - bipyridine, 97
  - carbohydrates, 87
  - carbon-carbon bond constructions, 76–77
  - catalytic improvements, 74–75
  - enantioselectivity, 75–76
  - five-membered heterocycles, 77–79
  - furanoenone, 96
  - historical background, 71
  - mechanisms, 71–72
  - microwave irradiation, 73–74
  - natural products, 90–95
  - phosphine ligands, 72–73
  - six-membered rings, 79–82
  - synthetic utility, 77–96
- Neuramidase inhibitors, Wohl-Ziegler reaction, 669
- Neutral pathways, Heck reaction, 5–7
- N*-Heterocyclic carbenes (NHC), Barton-McCombie deoxygenation, 625
- Nicholas reaction, organometallic reagents
- basic principles, 284
  - 6-bromo-4-ethynyl-3-(1-fluoro-1-methylethyl)chromane, 297
  - endocyclic intramolecular reactions, 292–293
  - exocyclic intramolecular reactions, 293–294
  - historical perspective, 284–285
  - intermolecular reactions, 290–291
  - mechanisms, 285–286
  - synthetic utility, 289–296
  - tandem reactions, 294–296
  - variations and improvements, 286–289
- Nicholas reaction, organometallic reagents, hexacarbonyl( $\mu$ -( $\eta^4$ -[2,4-dimethyl-2-(prop-2-yn-1-yl)]-8-oxabicyclo-[3.2.1]octan-3-one))dicobalt, 296–297
- Nickel catalysts
- Kumada cross-coupling
    - alkyl halides, 63–64
    - asymmetric reactions, 55–57
    - basic principles, 47–48
    - mechanisms, 49–52
    - standard procedures, 66–67

- Nickel catalysts (*continued*)  
  synthetic applications, 52–59  
  Negishi cross-coupling reactions  
    basic principles, 70  
    microwave irradiation, 73–74  
  Nozaki-Hiyama-Kishi reaction, 300–301  
    chiral oxazoline ligands, 303–307  
  Sonogashira reaction, 126–127  
  Stille coupling, 142  
    alkyl halide reactions, 148–149  
  Tsuji-Trost reaction, asymmetric allylic alkylation, 208  
  Ullmann coupling, 261  
Nickel(II)-phosphine complex, Kumada cross-coupling reactions, 49, 53–59  
Nitroaldo condensation, Henry reaction, 403–404  
Nitroalkanes, Henry reaction, 403–415  
Nitroalkenes, Henry reaction, 406–408  
*m*-Nitrocinnamic acid, Knoevenagel reaction, Verley-Doebner modification, 497  
Nitrogen nucleophiles, Tsuji-Trost reaction, 194  
 $\alpha$ -Nitroketones, Henry reaction, 410–411  
Nitronates, Henry reaction, 414  
Nitronc derivatives, Barton nitrite photolysis reaction, 643–644  
2-Nitro-2-propen-1-ol privalate (NPP), Henry reaction, 407–408  
6-Nitro-7-trimethylsilyloxytridecane, Henry reaction, 417  
*N*-methylmorpholine (NMM), Morita-Baylis-Hillman homologation, 356  
Nokami hydroxylative Knoevenagel reaction, mechanisms, 481–482  
Non-steroidal rigid systems, Barton nitrite photolysis reaction, 638–641  
Norpseudoephedrine derivative, Sakurai allylation reaction, *syn/anti* isomerism, 548–551  
Nozaki-Hiyama-Kishi reaction, organometallic reagents  
  basic principles, 299–300  
  bipyridyl ligands, 301–302  
  chiral oxazoline ligands, 303–304  
  chiral salen ligands, 302–303  
  drug discovery analogs, 314  
  (*Z*)-haloallylic alcohols, 308  
  historical perspective, 300  
  large-sized ring system cyclization, 307–308  
  mechanism, 300–301  
  miscellaneous reactions, 309  
  multidentate ligands, 303–307  
  natural products, 309–314  
    (*S*)-1-phenyl-3-butene-1-ol, 314–315  
  synthetic utility, 307–314  
  9-(*tert*-butyldimethylsilyloxy)-5,6,12,13-tetrahydro-8,9,10,11-tetrahydro-7*H*-benzo[11]annulen-7-ol, 315  
Olefins  
  Horner-Wadsworth-Emmons reaction, 424–429  
  Julia-Lythgoe olefination  
    acetoxy sulfone-vinyl sulfone conversion, 470  
    alkyl sulfone-aldehyde coupling, 469–470  
    basic principles, 446–447  
    historical perspective, 447–448  
    mechanism, 448–449  
    natural product synthesis, 459–469  
    synthetic utility, 450–459  
    vinyl sulfone reductive cleavage, 470–471  
  Negishi cross-coupling reaction, 84  
  Peterson olefination  
    basic principles, 520  
    experimental compounds, 534–536  
    historical perspective, 520–521  
    mechanism, 521–522  
    synthetic utility, 525–534  
    variations and improvements, 523–525  
  Stetter reaction, basic principles, 575  
  Tebbe methylenation, 321–327  
Olivine, Corey-Fuchs reaction, 398  
Organoboron compounds, Suzuki reaction  
  basic principles, 164–165  
  mechanisms, 165–168  
Organochromium(III) nucleophile, Nozaki-Hiyama-Kishi reaction, 300–301  
Organocopper reagents  
  Castro-Stephens reaction  
    allylic halides, 229–230  
    aryl halide alkylation, 224–225  
    basic principles, 212–214  
    catalytic mechanism and *in situ* acetylide formation, 218–220  
  Catiot-Chodkiewicz reaction, 221–223, 231  
  classical mechanism, 217–218  
  copper-catalyzed Sonogashira, 229

- copper(I) acetylide preparation, 231–232  
copper nanoclusters - heterogeneous catalysis, 228–229  
heterocycle synthesis, 226–227, 233  
historical perspective, 214–216  
ligand effects, 220–221  
macrocycle synthesis, 225–226  
methyl 2-(2-(5-(methoxycarbonyl)benzofuran-2-yl)ethyl)benzofuran-5-carboxylate, 234  
2-phenylfuro[3,2-b]pyridine, 233–234  
regioselectivity and stereoselectivity, 220  
Rosenmund-von Braun reaction, 223–224, 232  
silylated alkynes, 230  
*in situ* modification, 234  
synthetic utility, 224–227
- Glaser coupling**  
basic principles, 236  
9,9'-dianthryldiacetylene (Eglinton modification), 253  
1,4-di-(2'-quinoly)-1,3-butadiene (Cameron modification), 252–253  
2,4-hexadiyne-1,6-diol, 252  
historical perspective, 236  
mechanism, 236–237  
*N,N'*-phenylbuta-1,3-diyne-1,4-tosylamide (Hay modification), 253  
synthetic utility, 241–252  
variations and improvements, 238–241
- Ullmann coupling**  
asymmetric copper coupling, 265–266  
basic principles and historical perspective, 258  
intramolecular palladium coupling, 266  
mechanisms, 258–259  
synthetic utility, 262–265  
variations, improvements, or modifications, 259–261
- Organohalides, Negishi cross-coupling reactions, 75
- Organometallic reagents**  
Knoevenagel reaction, 483–484  
McMurry coupling  
basic principles, 268  
historical perspective, 268–272  
indole, 281  
mechanism, 273–276  
receptor, 281–282  
synthetic utility, 278–281  
variations, improvements, modifications, 276–278
- Nicholas reaction**  
basic principles, 284  
6-bromo-4-ethyl-3-(1-fluoro-1-methylethyl)chromane, 297  
endocyclic intramolecular reactions, 292–293  
exocyclic intramolecular reactions, 293–294  
historical perspective, 284–285  
intermolecular reactions, 290–291  
mechanisms, 285–286  
synthetic utility, 289–296  
tandem reactions, 294–296  
variations and improvements, 286–289
- Nozaki-Hiyama-Kishi reaction**  
basic principles, 299–300  
bipyridyl ligands, 301–302  
chiral oxazoline ligands, 303–304  
chiral salen ligands, 302–303  
drug discovery analogs, 314  
(*Z*)-haloallylic alcohols, 308  
historical perspective, 300  
large-sized ring system cyclization, 307–308  
mechanism, 300–301  
miscellaneous reactions, 309  
multidentate ligands, 303–307  
natural products, 309–314  
(*S*)-1-phenyl-3-butene-1-ol, 314–315  
synthetic utility, 307–314  
9-(*tert*-butyldimethylsilyloxy)-5,6,12,13-tetrahydro-8,9,10,11-tetrahydro-7*H*-benzo[1,1]annulen-7-ol, 315
- Tebbe methylenation**  
basic principles, 319  
historical perspective, 319–320  
mechanisms, 320–321  
Petasis olefination, 321–327  
Petasis-Tebbe procedural comparisons, 331  
synthetic utility, 327–331
- Organometallic reagents, Nicholas reaction,**  
hexacarbonyl( $\mu$ -( $\eta^4$ -[2,4-dimethyl-2-prop-2-yn-1-yl])-8-oxabicyclo-[3.2.1]octan-3-one))dicobalt, 296–297
- Organosilanes, Sakurai allylation reaction,** 562
- Organosiloxanes, Hiyama cross-coupling reaction,** 35–36

- Organosilyl precursors, Hiyama cross-coupling reaction, 38–39
- Organostannane, Stille coupling and activation of, 142–145
- toxicity reduction, 149–151
- Organotrifluoroborate reagents
- Suzuki coupling reactions, 171–178
  - Wittig reaction, 606
- Organozinc reagents, Negishi cross-coupling reactions, 70
- carbon–carbon bond formation, 75–76, 89
  - five-membered heterocycles, 77–79
- Oxacycle ring system, Morita-Bayless-Hillman reaction, 364
- Oxalate derivatives, Barton-McCombie deoxygenation, 618
- Oxaphosphetanes, Wittig reaction, 590
- Oxaphospholenes, Wohl-Ziegler reaction, 667
- Oxazoles, Negishi cross-coupling reactions, 78
- Oxazoline ligands, Nozaki-Hiyama-Kishi reaction, 303–307
- Oxidative addition, Stille coupling, mechanism, 136–139
- Oxygen nucleophiles, Tsuji-Trost reaction, 194–195
- asymmetric allylic alkylation, 198–199
- Palladacycles, Heck reactions, 22–23
- Palladium-carbon heterogeneity, Heck reactions, 25
- Palladium chemistry
- Heck reaction, 2–31
    - alternative solvents, 25–27
    - anionic pathways, 7–9
    - aqueous media, 25–26
    - asymmetric intermolecular reaction, 17
    - asymmetric intramolecular reaction, 13–17
    - basic principles, 2
    - carbenes, 23
    - cationic vs. neutral pathways, 5–7
    - conjugated systems, 19
    - fluorous systems, 27
    - Fu's experimental conditions, 30
    - high-activity ligands, 20–23
    - historical perspective, 2–3
    - ionic liquids, 26–27
    - Jeffery's experimental conditions, 30–31
    - leaving groups, 27
    - ligand-free catalysts, 11–12, 23–25
    - mechanisms, 3–12
    - metal catalysts, 28
    - palladacycles, 22–23
    - phosphines, 21–22
    - polymers, 20
    - reductive reactions, 28–29
    - regioselectivity and stereoselectivity, 9–10
    - supercritical fluids, 27
    - supported catalysts, 23–25
    - synthetic utility, 12–20
    - zipper reactions, 18
- Hiyama cross-coupling reaction, 33–45
- basic principles, 33
  - conjugate additions, 40–41
  - experimental compounds, 45
  - heterocycle examples, 39–40
  - historical perspective, 33–34
  - improvements, 36–38
  - mechanisms, 34–35
  - natural product applications, 43–44
  - organosiloxane preparations, 35–36
  - organosilyl precursors, 38–39
  - synthetic utility, 38–44
  - tandem reactions, 41–42
- Kumada cross-coupling reactions
- alkyl halides, 63–64
  - aryl tosylates, 60
  - asymmetric cross-coupling, 55–57
  - basic principles, 47–48
  - highly-active nickel-catalyzed procedure, 67
  - historical perspective, 48–49
  - Knochel-type Grignard reagents and triarylmagnesiates, 60–63
  - mechanisms of, 49–52
  - metallic catalysts, 64–66
  - natural product synthesis, 58–59
  - standard nickel-catalyzed procedure, 66–67
  - synthetic utility, 52–59
- Negishi cross-coupling reactions
- alkenes, alkynes, polyenes, enynes, 83–86
  - amides and esters, 89
  - amino acids, 87–89
  - basic principles, 70
  - bipyridine, 97
  - carbohydrates, 87
  - carbon-carbon bond constructions, 76–77
  - catalytic improvements, 74–75
  - enantioselectivity, 75–76
  - five-membered heterocycles, 77–79

- furanocyne, 96  
historical background, 71  
mechanisms, 71–72  
microwave irradiation, 73–74  
natural products, 90–95  
phosphine ligands, 72–73  
six-membered rings, 79–82  
synthetic utility, 77–96
- Sonogashira reaction  
alkyne homocoupling and acetylene reactivity, 109–110  
aqueous solvent reactions, 127–128  
basic principles, 100–102  
bioconjugates, 121–122  
bulky phosphine ligand, copper-free conditions, 129–130  
complex fragment coupling, 111–114  
copper co-catalyst, 104–106  
copper-free mechanism, 106–107  
cylindramide intermediate, 129  
electronic and optical properties of compounds, 117–118  
fatty acids and polyunsaturated systems, 114–115  
heterocycle synthesis, 118–121  
heterogeneous catalysts, 109  
historical perspective, 102–103  
ligand activity, 123–125  
ligand-free catalysts, 108, 125–127  
mechanisms, 107–108  
metal catalysts, 128  
non-traditional coupling partners, 128  
polymers, 122–123  
regioselectivity and stereoselectivity, 108  
self-assembly subunits, dendrimers, and biopolymers, 115–117  
synthetic utility, 110–123
- Stille coupling  
additives, 140–142  
alkyl halide catalytic development, 147–149  
aryl chloride catalyst development, 145–147  
basic principles, 133–134  
carbonylative coupling, 158  
historical perspective, 134–136  
large-scale coupling, 159  
ligand influences, 139–140  
mechanisms of, 136–139  
organostannane activation, 142–145  
 $\pi$ -allyl Stille coupling, 158–159  
Stille-Kelly reaction, 151–152  
synthetic utility, 152–156  
tin compound toxicity, 149–151  
toxicity management, 156–157  
unactivated secondary alkyl halides, 157
- Suzuki reaction  
aryl chlorides, 169–170  
basic principles and trends, 163  
1-(4-benzylphenyl)ethanone, 181  
comparisons with other cross-coupling reactions, 163–165  
enantioselective reactions, 174–176  
heteroaromatic compounds, 170–171  
highly active catalysts, 168–169  
historical perspective, 165–166  
mechanism, 166–168  
5-(2'-methylphenyl)-1*H*-indole, 180–181  
organotrifluoroborate reagents, 171–173  
synthetic utility, 176–180  
unactivated alkyl halides and sulfonates, 173–174
- Tsuji-Trost reaction  
alcohol oxidation, 204–205  
allylic compound hydrogenolysis, 205–206  
amine nucleophiles, 199–201  
asymmetric allylic alkylation, 188–190  
basic principles, 185  
6,6-bis-phenylsulfonyl-4-(*tert*-butyldimethylsilyloxymethyl)-1-(4-methoxy-benzyloxy)-hex-3-en-2-ol, 209  
carbon nucleophiles, 192–193, 196–197  
carbonylation, 202–203  
conjugated diene formation, 203–204  
“hard” carbon nucleophiles, 195–196  
historical perspective, 186  
mechanisms, 186–190  
metal catalysts, 206–208  
nitrogen nucleophiles, 194  
oxygen nucleophiles, 194–195, 197–198  
(2*S*,5*S*)-2-[3'-phenylsulfonyl-*N'*-(4-methoxybenzyl)succinimid-3'-yl]-5-benzyloxy-2,5-dihydrofuran, 209  
“soft” carbon nucleophiles, 190–193  
sulfur nucleophiles, 201  
synthetic utility, 190–201  
2-(trimethylsilylmethyl)allyl acetate, 201–202
- Palladium-free Sonogashira reaction, 128, 229  
Palominol, Stille coupling, 154

- Pearlman's catalyst, Henry reaction, alcohols, 411–412
- (*S*)-[6,6'-(2*R*,4*R*-Pentadioxyl)]-(2,2')-bis(diphenylphosphoryl)-(1,1')-biphenyl, Ullman coupling, 265–266
- PEPPSI-Ipr precatalyst, Negishi cross-coupling reactions, 74–75
- Perhydrohistrionicotoxin, Barton nitrite photolysis reaction, 638–639
- Peridinin, Julia Kocienski/Julia Lythgoe olefination, 461–462
- Peroxisome proliferator-activated receptors (PPARs), Knoevenagel reaction, 493
- Petasis reagent, Tebbe methylation, 321–327  
carbonyl compounds, 328–331  
general procedure, 331
- Peterson olefination  
basic principles, 520  
experimental compounds, 534–536  
historical perspective, 520–521  
mechanism, 521–522  
synthetic utility, 525–534  
variations and improvements, 523–525  
Wittig reaction modification, 603
- Ph<sub>3</sub>C<sub>2</sub>O<sub>2</sub>Ag, Arndt-Eistert homologation via acid chloride, 347–348
- (Phenoxy)thiocarbonate derivatives, Barton-McCombie deoxygenation, 616
- N,N'*-Phenylbuta-1,3-diyne-1,4-tosylamide (Hay modification), Glaser coupling, 253
- (*S*)-1-Phenyl-3-butene-1-ol, Nozaki-Hiyama-Kishi reaction, 314–315
- 2-Phenylfuro[3,2-*b*]pyridine, Castro-Stephens reaction, 233–234
- 1-Phenyl-1,4-pentanedione, intermolecular Stetter reaction, 583–584
- Phenylsulfonyl group, Nakami hydroxylative Knoevenagel reaction, 481–482
- (2*S*,5*S*)-2-[3'-Phenylsulfonyl-*N'*-(4-methoxybenzyl)succinimid-3'-yl]-5-benzoyloxy-2,5-dihydrofuran, Tsuji-Trost reaction, 209
- Phomaactins, Nozaki-Hiyama-Kishi reaction, 310
- Phorbexazoles  
Horner-Wadsworth-Emmons reaction, 441–443  
Nozaki-Hiyama-Kishi reaction, 311
- Phosphazenes, Wittig reaction modification, 601
- Phosphine-boranes, Barton-McCombie deoxygenation, phosphorous-based reductants, 623
- Phosphines  
Castro-Stephens reaction, catalytic mechanism, 220  
Heck reactions, 21–22  
Negishi cross-coupling reactions, 72–73  
Sonogashira reaction  
bulky ligand condition, 129  
high-activity ligands, 124–125  
Stille coupling, 139–140  
alkyl halide reactions, 148–149  
Wittig reaction, 592–603
- Phosphodiesterase inhibitor, Knoevenagel reaction, 494
- Phosphonamides, Wittig reaction, 593–603
- Phosphonate 99, Horner-Wadsworth-Emmons reaction, 444
- Phosphonates  
Horner-Wadsworth-Emmons reaction, 422–423  
Wittig reaction variants, 598
- Phosphorous compounds  
Barton-McCombie deoxygenation, phosphorous-based reductants, 622–623  
Peterson olefination, 520–521  
Wittig reaction modification, 595–603
- Pinacol step, McMurry coupling, 273–276  
variations and improvements, 276–278
- $\pi$ -allyl Stille coupling, 158–159
- (-)-Pironectin, Mukaiyama addol reaction, 506
- Platinum catalysts, Tsuji-Trost reaction, asymmetric allylic alkylation, 208
- Pheamine, Morita-Bayless-Hillman reaction, 368
- Polyacetylenes, Glaser coupling, organocopper reagents, 246–252
- Polycavernoside A  
Horner-Wadsworth-Emmons reaction, 437–438  
Nozaki-Hiyama-Kishi reaction, 313
- Polyenes  
asymmetric intramolecular Heck reaction, cyclization, 16–17  
Negishi cross-coupling reaction, 83–86  
Suzuki coupling reactions, 176–177
- Polymers  
Barton-McCombie deoxygenation, tin-based reductants, 619  
Heck reactions, 20

- Sonogashira reaction, 122–123
- Polymethylhydrosiloxane (PMHS), Stille coupling, 151
- Poly(methyl)hydrosiloxane (PMHS), Barton-McCombie deoxygenation, tin-based reductants, 618–619
- Polyunsaturated systems, Sonogashira reaction, 114–115
- Polyurethanes, Barton nitrite photolysis reaction, 644
- Potassium organotrifluoroborate salts, Suzuki coupling reactions, 177–178
- Potassium phosphate, Henry reaction, acetonitrile, 415
- P(o-Tol)*, Heck reactions, 21–22
- Precatalysts, Heck reaction, anionic pathways, 7–9
- Pregnene, Wohl-Ziegler reaction, 669
- Prins cyclization reaction, Peterson olefination and, 532
- Promoters
- Knoevenagel reaction, 483–484
  - Sakurai allylation reaction
    - chiral promoters, 556–557
    - overview, 538–539
- 2-Propanol, Barton-McCombie deoxygenation, 624–625
- Propargyl alcohol, Castro-Stephens reaction, Cadiot-Chodkiewicz reaction and, 231
- Propargylsilane, Corey-Fuchs reaction, 397–398
- Prostaglandins, Julia Kocienski/Julia-Lythgoe olefination, 459–460
- Protein kinase C (PKC), Negishi cross-coupling reactions, 95
- Protic solvents, Morita-Baylis-Hillman reaction, 352–353
- Pseudohalides, Negishi cross-coupling reactions, 75
- Pseudopteraxazole, Sandmeyer reaction, 653
- Pybox catalyst, Sakurai allylation reaction, 558
- Pyridazine, Negishi cross-coupling reactions, 80–81
- Pyridines
- Castro-Stephens reaction, 213–214
  - Knoevenagel reaction, Verley-Doebner modification, 480–481
  - Negishi cross-coupling reactions, 80
- Pyridoncarboxylic acids, Sandmeyer reaction, 653–654
- Quadrigemine, asymmetric intramolecular Heck reaction, 13–17
- (–)-Quinocarcin, Wittig reaction modification, 602
- Quinuclidine catalysts, Morita-Baylis-Hillman reaction, 352–353
- Radical chemistry
- Barton-McCombie deoxygenation
    - basic principles, 613
    - 4,6-dimethoxy-1-(tetradec-13'-enyl)-1*H*-indole, 630
    - historical perspective, 613–614
    - mechanisms, 614–616
    - miscellaneous alternative reductants, 623–625
    - phosphorous-based reductants, 622–623
    - silicon-based reductants, 619–621
    - synthetic utility, 625–629
    - 1,1'-thiocarbonyldiimidazole, 629–630
    - tin-based reductants, 618–619
    - variation and improvements, 616–618
  - Barton nitrite photolysis reaction
    - basic principles, 632
    - flexible molecule functionalization, 642
    - historical perspective, 632–634
    - 9-hydroxy-2,2,4,8-tetramethyl-octahydro-4,8-methano-azulen-1-one oxime, 645
    - mechanisms, 634
    - non-steroidal rigid system functionalization, 638–642
    - steroid core functionalizations, 635–638
    - synthetic utility, 634–642
    - variations and improvements, 642–644
  - Sandmeyer reaction
    - basic principles, 647
    - bromination, 655
    - chlorination, 655–656
    - cyanation, 656–657
    - historical perspective, 647–648
    - hydroxylation, 657
    - iodination, 657
    - mechanism, 648
    - medicinal and heterocyclic chemistry, 653–654
    - natural product synthesis, 650–653
    - variations, 649–650
  - Wohl-Ziegler reaction
    - alternative solvents, 671–672

- Radical chemistry (*continued*)  
  basic principles, 660  
  (*R*)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, 672  
  halogenating agents, 671  
  historical perspective, 660–661  
  initiators, 670–671  
  mechanisms, 661–668  
  regioselectivity and stereoselectivity, 664–668  
  synthetic utility, 668–670
- Raf kinase, Negishi cross-coupling reactions, 95
- Ragoussis modification, Knoevenagel reaction  
  (*E*)-dec-3-enoic acid, 497  
  Verley-Doebner modification, 479–481
- Rapamycin, Stille coupling in, 152–153
- Reactivity pathway, copper-free Sonogashira reaction, 106–107
- Receptor structures, McMurry coupling, 281–282
- Redox-active molecular wires, Corey-Fuchs reaction, 400–401
- Reductive cleavage, Julia–Lythgoe olefination, vinyl sulfones, 470–471
- Reductive Heck reactions, palladium compounds, 28–29
- Regioselectivity  
  Castro-Stephens reaction, 220  
  Heck reaction, 9–10  
    cationic pathways, 6–7  
  Sonogashira reaction, 108  
  Tsuji–Trost reaction, 187–188  
    carbon nucleophiles, 191–193  
  Wohl–Ziegler reaction, 664–668
- Reidispongiolide A, Nozaki-Hiyama-Kishi reaction, 311
- Retro-Henry reaction, 415
- ( $\pm$ )-Ricciocarpin A, Barton-McCombie deoxygenation, 627
- Ring systems  
  Homer-Wadsworth-Emmons reaction, 423  
  Nozaki-Hiyama-Kishi reaction, cyclization, 307  
  Sandmeyer reaction, natural product synthesis, 650–653
- Rishitin, Barton nitrite photolysis reaction, 639
- Rosenmund-von Braun reaction, Castro-Stephens reaction and organocopper reagents, 223–229  
  related processes, 232
- Roscophilin, Negishi cross-coupling reactions, 92–93
- Rotaxanes, Glaser coupling, organocopper reagents, 249–252
- Roush reaction  
  Sakurai allylation reaction, 567  
  Wittig reaction variants, 596–603, 604
- Sakurai allylation reaction  
  1,2-asymmetric induction, 551–553  
  1,3-asymmetric induction, 554  
  asymmetric catalytic reactions, 555–559  
  basic principles, 538–539  
   $BI_3$  promoter, 569  
  chiral silane chirality transfer, 554–555  
  crotylsilanes, 567–568  
  *E/Z* isomerism, 547  
   $FeCl_3$  promoter in  $MeNO_2$ , 571–572  
  historical perspective, 539–540  
  mechanism, 540–546  
    aldehyde substituents, 545  
    Lewis acid-carbonyl complex, 542–545  
    silane substituents, 545–546  
   $SnCl_4$  promoter, 569–570  
  *syn/anti* isomerism, 547–551  
  synthetic utility, 560–567  
  synthons, 559–560  
   $TiCl_4$  promoter, 568–570  
   $ZnCl_2$  promoter, 570–571
- Salen ligands  
  Mukaiyama aldol reaction, enantioselectivity, 516–517  
  Nozaki-Hiyama-Kishi reaction, 302–303
- Salinosporamide A, Morita-Bayless-Hillman reaction, 370–371
- Sandmeyer hydroxylation reaction, 649–650
- Sandmeyer reaction  
  basic principles, 647  
  bromination, 655  
  chlorination, 655–656  
  cyanation, 656–657  
  historical perspective, 647–648  
  hydroxylation, 657  
  iodination, 657  
  mechanism, 648  
  medicinal and heterocyclic chemistry, 653–654  
  natural product synthesis, 650–653

- variations, 649–650
- Santiagonamine, Ullman coupling reaction, 263
- Scyphostatin, Negishi cross-coupling reactions, 91
- Sec-alkylmethylphosphinates, Barton-McCombie deoxygenation, 625
- Selenoamides, Peterson olefination, 529
- Self-assembly subunits, Sonogashira reaction, 115–117
- Seychelogenin, Barton nitrite photolysis reaction, 636
- Silane substituents
  - Barton-McCombie deoxygenation, silicon-based reductants, 619–621
  - Sakurai allylation reaction
    - chirality transfer, 554–555
    - Lewis acid-carbonyl complex, 545–546
    - synthons, 559–560
- Sila-Stetter reaction, 578–579
  - intermolecular variants, 584–585
- Silenes, Peterson olefination, 529
- Silicon compounds
  - Barton-McCombie deoxygenation, silicon-based reductants, 619–621
  - Peterson olefination, 520–521
- Silver ions, McMurry coupling, 280–281
- Silylated alkynes, Castro-Stephens reaction, 230
- $\alpha$ -Silylcarbanion, Wittig reaction modification, 603
- Silyl enol ether, Mukaiyama aldol reaction, 504–505
- Silyl nitro addition, Henry reaction, 416–417
- Silylnitronate, Henry reaction, 416
- Silyl transfer
  - Mukaiyama aldol reaction, 502–503
  - Sakurai allylation reaction, Lewis acid-carbonyl complex, 545–546
- Six-membered rings, Negishi cross-coupling reactions, 79–82
- SNF 4435 compounds, Horner-Wadsworth-Emmons reaction, 433
- “Soft” nucleophiles, Tsuji-Trost reaction
  - basic mechanism, 187–188
  - carbon nucleophiles, 190–193
- Solandelactones E and F, Nozaki-Hiyama-Kishi reaction, 311
- Solid-phase chemistry, Stille coupling, toxicity reduction, 149–150
- Solid-phase organic synthesis (SPOS), Horner-Wadsworth-Emmons reaction, 424–429
- Solvents
  - Heck reactions, 25–27
  - Morita-Baylis-Hillman reaction, 353–358
  - Stille coupling, 148–149
  - Wohl-Ziegler reaction
    - alternative solvents, 671–672
    - mechanisms, 662–668
- Sonication, McMurry coupling, 272
- Sonogashira coupling reaction
  - Castro-Stephens reaction and, 213–214
  - Corey-Fuchs reaction, 400–401
  - palladium chemistry
    - alkyne homocoupling and acetylene reactivity, 109–110
    - aqueous solvent reactions, 127–128
    - basic principles, 100–102
    - bioconjugates, 121–122
    - bulky phosphine ligand, copper-free conditions, 129–130
    - complex fragment coupling, 111–114
    - copper co-catalyst, 104–106
    - copper-free mechanism, 106–107
    - cylindramide intermediate, 129
    - electronic and optical properties of compounds, 117–118
    - fatty acids and polyunsaturated systems, 114–115
    - heterocycle synthesis, 118–121
    - heterogeneous catalysts, 109
    - historical perspective, 102–103
    - ligand activity, 123–125
    - ligand-free catalysts, 108, 125–127
    - mechanisms, 107–108
    - metal catalysts, 128
    - non-traditional coupling partners, 128
    - polymers, 122–123
    - regioselectivity and stereoselectivity, 108
    - self-assembly subunits, dendrimers, and biopolymers, 115–117
    - synthetic utility, 119–123
- Spiculoic acid, Wittig reaction, 607
- (–)-Spinosyn A, Morita-Bayless-Hillman reaction, 368
- Spirobis lactone, Tebbe methylenation, 322–327
- Spirotyrptostatin A,
  - Julia-Kocienski/Julia-Lythgoe olefination, 467

- Spongistatin, Mukaiyama aldol reaction, 506–507
- S• radicals, Wohl-Ziegler reaction, 662–668
- Stannic chloride (SnCl<sub>4</sub>) promoter, Sakurai allylation reaction
- basic properties, 538–539
  - example, 569–570
  - Lewis acid-carbonyl complex, 543–544
- Stereochemistry
- Knoevenagel reaction, 487
  - Mukaiyama aldol reaction, 504
  - Wittig reaction, 591
    - Schlosser modification, 595–596
- Stereoselectivity
- Castro-Stephens reaction, 220
  - Heck reaction, 9–10
  - Kumada cross-coupling reactions, 49–52
  - Mukaiyama aldol reaction, 508–509
  - Sonogashira reaction, 108
  - Wohl-Ziegler reaction, 664–668
- Steric factors, Sakurai allylation reaction, Lewis acid-carbonyl complex, 543
- Steroid nitrites, Barton nitrite photolysis reaction, mechanism, 634–638
- Steroid synthesis, Barton nitrite photolysis reaction, 635–638
- Stetter reaction
- asymmetric intramolecular annulation, 585
  - basic principles, 575
  - biomimetic reactions, 578
  - enantioselective reactions, 579–583
  - historical perspective, 575
  - intermolecular reactions, 576–580, 583–585
  - intramolecular reactions, 580–582, 584
  - mechanism, 575–576
  - NaCN-catalyzed intermolecular reaction, 583–584
  - Sila-Stetter reaction, 578–579, 584–585
  - synthetic utility, 576–582
  - thiazolidine-catalyzed intermolecular reaction, 584
- Stille coupling, palladium chemistry
- additives, 140–142
  - alkyl halide catalytic development, 147–149
  - aryl chloride catalyst development, 145–147
  - basic principles, 133–134
  - carbonylative coupling, 158
  - historical perspective, 134–136
  - large-scale coupling, 159
  - ligand influences, 139–140
  - mechanisms of, 136–139
  - organostannane activation, 142–145
  - $\pi$ -allyl Stille coupling, 158–159
  - Stille-Kelly reaction, 151–152
  - synthetic utility, 152–156
  - tin compound toxicity, 149–151
  - toxicity management, 156–157
  - unactivated secondary alkyl halides, 157
- Stille-Hegedus synthesis, jatrophone compound, 153
- Stille-Kelly reaction, 151–152
- Still-Gennari reaction
- Horner-Wadsworth-Emmons reaction
    - mechanisms, 423–424
    - natural products, 429–443
    - synthetic procedures, 429
    - Wittig reaction modification, 594–595
- Still-Gennari reactions, Horner-Wadsworth-Emmons reaction, basic principles, 420–421
- “Stitching” techniques, Stille coupling, 152–156
- Stroke therapy
- Corey-Fuchs reaction, amide compounds, 398–399
  - Knoevenagel reaction, 493–494
- (-)-Subincanadines A and B, Nozaki-Hiyama-Kishi reaction, 314
- Sulfonates, Suzuki coupling reactions, 173–174
- Sulfones, Julia-Lythgoe olefination, 451–459
- Sulfoxides, Julia-Lythgoe olefination, 451–459
- Sulfur nucleophiles, Tsuji-Trost reaction, 201
- Sulfur-tin bonds, Barton-McCombie deoxygenation, 614–616
- Supercritical fluids, Heck reactions, 27
- Suzuki reaction
- palladium chemistry
    - aryl chlorides, 169–170
    - basic principles and trends, 163
    - 1-(4-benzylphenyl)ethanone, 181
    - comparisons with other cross-coupling reactions, 163–165
    - enantioselective reactions, 174–176
    - heteroaromatic compounds, 170–171
    - highly active catalysts, 168–169
    - historical perspective, 165–166
    - mechanism, 166–168
    - 5-(2'-methylphenyl)-1*H*-indole, 180–181
    - organotrifluoroborate reagents, 171–173

- synthetic utility, 176–180
- unactivated alkyl halides and sulfonates, 173–174
- Ullmann coupling and, 262
- syn*- $\beta$ -Hydride elimination, Heck reaction, regioselectivity and stereoselectivity, 10
- Syn* coordination, Sakurai allylation reaction, 544
- syn/anti* isomerism, 547–551
- Synthons, Sakurai allylation reaction, 559–560
- Syributin 1, Morita-Bayless-Hillman reaction, 365
- TADDOL-derived catalyst, enantioselective cross-benzoin condensation, 384–385
- Takeda alkylidenation, Tebbe methylenation, 326–327
- Tamoxifen compounds
  - McMurry coupling, 279–280
  - Wittig reaction variants, 598
- Tandem reactions
  - Hiyama cross-coupling reaction, 41–42
  - Knoevenagel reaction, 487–488
    - Diels-Alder reaction, 488–489
    - electrocyclization, 489–490
    - Knoevenagel-Mislow-Evans, 490–491
  - Mukaiyama aldol reaction, 511–512
  - Nicholas reaction, 294–296
- Tautomycin, Mukaiyama aldol reaction, 508–509
- Tebbe methylenation
  - organometallic reagents
    - basic principles, 319
    - historical perspective, 319–320
    - mechanisms, 320–321
    - Petasis olefination, 321–327
    - Petasis-Tebbe procedural comparisons, 331
    - synthetic utility, 327–331
  - Wittig reaction modification, 605
- Tedanolide, Horner-Wadsworth-Emmons reaction, 431
- Teicoplanin aglycon, Sandmeyer reaction, 651
- Terpene synthesis, Barton nitrite photolysis reaction, 638–641
- $\beta$ -*tert*-Butyldiphenylsilylketone, Peterson olefination, 526
- 9-(*tert*-Butyldimethylsilyloxy)-5,6,12,13-tetrahydro-8,9,10,11-tetrahydro-7*H*-benzo[11]annulen-7-ol, Nozaki-Hiyama-Kishi reaction, 315
- (*S*)-3-(*tert*-Butyloxycarbonylamino)-1-diazo-4-phenylbutan-2-one, Arndt-Eistert homologation, 346
- (*S*)-3-(*tert*-Butyloxycarbonylamino)-4-phenylbutanoic acid, Arndt-Eistert homologation, 346–347
- Tethered bis-(8-quinolinolato)-f(TBOx) chromium complex, Nozaki-Hiyama-Kishi reaction, 303
- Tetrabutylammonium peroxydisulfate, Barton-McCombie deoxygenation, 623–624
- Tetraethynylethene, Negishi cross-coupling reaction, 86
- Tetrahydrocannabinol, Kumada cross-coupling reactions, 59
- Tetrahydropyranes, Sakurai allylation reaction, 565–566
- THF-*N*-ethylpyrrolidinone (NEP) solvent, Negishi cross-coupling reactions, 74
- Thiamine diphosphate (ThDP), benzoin condensation, enantioselective dimerization, 383
- (+)-Thiazinotrienomycin, Julia-Kocienski/Julia-Lythgoe olefination, 463–464
- Thiazolium precatalyst, Stetter reaction, 575–576
- Thiazolylidine, intermolecular Stetter reaction, 584
- 2-Thiazolyliane species, Negishi cross-coupling reactions, 78–79
- Thioacetals, Tebbe methylenation, 326–327
- Thiocarbenates, Barton-McCombie deoxygenation, 615–618
  - 4,6-dimerhoxy-1-(10'-(*N*-imidazolylthiocarbonyloxy)-tetradec-13'-onyl)-1*H*-indole, 629–630
  - miscellaneous reductants, 624–625
  - tin-based reductants, 618–619
- Thioformate synthesis, Barton-McCombie deoxygenation, 617–618
- Thionyl chloride, Arndt-Eistert homologation, 335–337
- Thiophosphonate, Wittig reaction, 594–603
- Tin compounds, Barton-McCombie deoxygenation
  - sulfur-tin bonds, 614–616
  - tin-based reductants, 618–619
- Titanium-aluminum complex, Tebbe methylenation
  - basic properties, 319

- Titanium-aluminum complex, Tebbe methylenation (*continued*)  
historical perspective, 319–320
- Titanium carbene complex, Tebbe methylenation, 327
- Titanium compounds  
McMurry coupling, 271–272  
mechanistic pathways, 274–276  
variations and improvements, 277–278
- Merita-Baylis-Hillman homologation, 357–358  
intermolecular reactions, 376
- Mukaiyama aldol reaction, enantioselectivity, 515–517
- Titanium tetrachloride (TiCl<sub>4</sub>) promoter, Sakurai allylation reaction  
basic properties, 538–539  
example, 568–569  
Lewis acid-carbonyl complex, 543–544  
limitations, 570
- Titanocene complexes, Tebbe methylenation, 324–327
- Titanocene methylenation, Tebbe methylenation, 320–321
- Toxicity reduction, Stille coupling  
techniques for, 156–157  
tin compounds, 149–151
- (=)-Trachyspic acid, Nozaki-Hiyama-Kishi reaction, 314
- Transmetalation pathways, Stille coupling, 139
- Triarylmagnesiates, Kumada cross-coupling, 60–63
- Triazines, Sandmeyer reaction, 649–650
- Tricycloillicinone, Barton-McCombie deoxygenation, 626
- Tridentate ligands, Mukaiyama aldol reaction, enantioselectivity, 515–517
- Triene (1)-126, Julia-Lythgoe olefination, 471
- Trimethylsilyl-diazomethane, Arndt-Eistert homologation, 344–345
- $\gamma$ -(Trimethylsilyl)allylboranes, Peterson olefination, 533–534
- 2-(Trimethylsilylmethyl)allyl acetate, Tsuji-Trost reaction, 201–202
- 1,2,4-Triphenylbutane-1,4-dione, Stetter reaction, 585
- Triphenylphosphine-based catalysts, Suzuki coupling reactions, 168–169
- Tris(pentafluorophenyl)borane (TPPB), Mukaiyama aldol reaction, vinylogous variant, 510–511
- Tris(trimethylsilylmethyl)alane (TTMA), Peterson olefination, 525
- Triynes, Negishi cross-coupling reaction, 86
- Tsuji-Trost reaction, palladium chemistry  
alcohol oxidation, 204–205  
allylic compound hydrogenolysis, 205–206  
amine nucleophiles, 199–201  
asymmetric allylic alkylation, 188–190  
basic principles, 185  
6,6-bis-phenylsulfonyl-4-(*tert*-butyldimethylsilyloxymethyl)-1-(4-methoxy-benzyloxy)-hex-3-en-2-ol, 209  
carbon nucleophiles, 196–197  
carbonylation, 202–203  
conjugated diene formation, 203–204  
“hard” carbon nucleophiles, 195–196  
historical perspective, 186  
mechanisms, 186–190  
metal catalysis, 206–208  
nitrogen nucleophiles, 194  
oxygen nucleophiles, 194–195, 197–198  
(2*S*,5*S*)-2-[3'-phenylsulfonyl-*N'*-(4-methoxybenzyl)succinimid-3'-yl]-5-benzoyloxy-2,5-dihydrofuran, 209  
“soft” carbon nucleophiles, 190–193  
sulfur nucleophiles, 201  
synthetic utility, 190–201  
2-(trimethylsilylmethyl)allyl acetate, 201–202
- 6-Tuliposide B, Morita-Bayless-Hillman reaction, 363–364
- Turn-over number (TON)  
Heck reactions, 21–22  
Sonogashira reaction, 107–108  
polymers, 122–123
- Ullmann coupling, organocopper reagents  
asymmetric copper coupling, 265–266  
basic principles and historical perspective, 258  
intramolecular palladium coupling, 266  
mechanisms, 258–259  
synthetic utility, 262–265  
variations, improvements, or modifications, 259–261
- 2,5-Undecanedione, intermolecular Stetter reaction, 584
- Urea catalysts, Morita-Bayless-Hillman homologation, 359–360

- Urotropine, Morita-Baylis-Hillman homologation, 356
- (1)-U-106305, Julia-Kocienski/Julia-Lythgoe olefination, 465
- VEGFR kinase inhibitor, Stille coupling, 156
- Verley-Doebner modification, Knoevenagel reaction, 478-481, 497
- amino acid catalysis, 482-483
- m*-nitrocinnamic acid, 497
- Vinblastine
- Sonogashira reaction, 112-113
- Ullmann coupling, 261
- Vincristine, Ullmann coupling, 261
- Vinylogous lactone, Tebbe methylation, 322-327
- Vinylogous Mukaiyama aldol reaction, 509-511
- Vinylsilanes, Peterson olefination, 524-525
- Vinylstannanes, Stille coupling, 155
- Vinyl sulfone, Julia-Lythgoe olefination, acetoxy sulfone conversion, 470
- Vitamin D derivatives
- Barton nitrite photolysis reaction, 641-642
- Negishi cross-coupling reactions, 94-95
- Weinreb amides, Wittig reaction, 606-607
- Wittig reaction
- carbon-chain homologations
- basic principles, 587
- ethyl cyclohexylideneacetate, 609
- historical perspective, 587-588
- mechanism, 588-592
- methylene-cyclohexane, 608-609
- synthetic utility, 603-608
- variations, improvements, and modifications, 592-603
- Corey-Fuchs reaction, 393
- Peterson olefination, 520-521
- Sonogashira heterocycle coupling, 120-121
- Wohl-Ziegler reaction
- alternative solvents, 671-672
- basic principles, 660
- (*R*)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, 672
- halogenating agents, 671
- historical perspective, 660-661
- initiators, 670-671
- mechanisms, 661-668
- regioselectivity and stereoselectivity, 664-668
- synthetic utility, 668-670
- Wolf rearrangement, Arndt-Eistert homologation
- $\beta$ -amino acid synthesis, 337-338
- basic principles, 335-337
- miscellaneous compounds, 342-343
- Xanthates, Barton-McCombie deoxygenation
- phosphorous-based reductants, 623
- silicon-based reductants, 620-621
- Xerulinic acid, Negishi cross-coupling reactions, 93-94
- Ylide carbanion structures, Wittig reaction, 588
- variations, improvements or modifications, 592-603
- Ynolate anions, Arndt-Eistert homologation, 345-346
- (*S*)-Zearalenone, Stille coupling and, 1550
- Ziegler-Ullman reaction, organocopper reagents, 262-263
- Zinc complexes
- Henry reaction, 409
- Mukaiyama aldol reaction, enantioselectivity, 514-517
- Sakurai allylation reaction,  $ZnCl_2$  promoter, 570-571
- Sandmeyer reaction, 649-650
- Zipper reactions, Heck cascade, 18
- Zwitterion compounds, Morita-Baylis-Hillman reaction, 351-353