

Index

a

- Abbasov/Romo's Diels–Alder
lactonization 628
- ab initio
– calculations 1159
– molecular orbital calculations 349
– wavefunction 209
- acceptor-substituted benzhydrylium ions 94
- ACC processes 545
- acetate/enolate exchange 437, 474
- acetonitrile 771
– benzhydrylium ions 96
– tertiary amines reactions 100
- acetophenones 298, 300, 395, 409, 411, 417, 421
- α -acetoxy allylsilane 259
- α -acetoxy β -amino acid derivatives 1101, 1102
- 2-(acetoxymethyl)-2,3-butadienoates 759, 760
- acetoxy-substituted α,β -unsaturated ketones 263
- acetylation 131, 132, 138
- acetyl cation affinities (ACA) 128
- N*-acetyl colchicolin 1106, 1107
- acetyl cyclobutadienyl iron tricarbonyl complex 425
- N*-acetyl cysteine methyl ester catalyst 700
- acetyl phosphate hydrolysis 23
- N*-acetylpyridinium intermediates 21
- O*-acetylquinine 528
- achiral bicyclic triazolium salts 511
- achiral cyclic silyl ketene acetals 505
- achiral Lewis base catalysts 141
- achiral NHC-based acylating agent 514
- achiral NHC-catalyzed reactions 1312
– of cyclopropane aldehydes 513
- achiral phosphoramides 327
- achiral sulfur electrophiles 1173
- Achmatowicz reaction 447
- acid–base interaction 33, 41, 61, 62, 72, 76
- acid–base theory 15, 16, 199
- acid chlorides 463, 542, 543, 545, 553, 583, 584
– Lewis base base-catalyzed enantioselective α -chlorination of 596
- acidic cocatalysts
– effect of 810–813
– iminium ion 811
- acidic trifluoroethyl thiol esters 1062
- acids/bases
– electronic theory of 35
– Lewis definition, extensions, expansions of, and objections 35
- acrylates 197, 201, 203, 222, 791
– enantioselective β -ICD-promoted reactions 671
– β -functionalization
– – mechanism of 1318
– β -ICD-catalyzed reactions 670
– S_N2' – S_N2' displacement, synthesis of 765
– β' -umpolung reaction, preparation of 759
- acrylonitriles 191, 195, 196, 210, 540
– Basavaiah's RC dimerizations of 690
– hexamerization 716
– polymerization process 195
- γ -activation 755
- acyclic β -boryl esters 977
- acyclic *E*-enol ether 321
- acyclic ethyl ketone-derived enol ethers 313, 317
- acyclic ketones 304, 1061
– derived enol ethers 317
- N*-acyl- α -chloroglycines 565
- N*-acyl aminophosphine 783
- acylammonium 553, 572, 591
– X-ray analysis 614
- N*-acylammonium acyl donors 628
- N*-acylammonium salt 528, 531, 615, 627
– ^{13}C NMR comparison of 627

- acyl anion equivalent
 - vs. homoenolate pathways with isatin-derived ketimines 1329
 - vs. homoenolate reactivity with nitroalkenes 1328
- N*-acylation 459, 514
 - amidine- and isothioureia-derived catalysts 505
- O*-acylation 474, 486
- acylations 96, 129, 131, 139, 141, 459, 474, 486
 - catalyst 477
 - of HBTM-2.1 572
 - KR of sec-benzylic alcohols 509
 - rates 136
 - of secondary alcohol 131
 - of tosylhydrazide with anhydride reagents 141
- acyl azolium 1324
 - precursors 1320
- acyl chlorides 538
 - electrophiles 474
- acyl donors, influence of 132–136
- acyl halide-aldehyde cyclocondensation (AAC) 545, 546
- N*-acylhydrazones 1030
- acylhydrazones, allylation of 1030
- N*-acyloxazolidinones 978
- α -acyloxyacroleins
 - Diels–Alder reaction of 842, 843
- α -acyloxy-allylsilane 258, 937
 - to α,β -unsaturated ketones 937
- acyl-phosphonium salt 461
- acyl pyridinium–alkylcarbonate ion pair 135
- N*-acylquinolinium salt 1227
- N*-acyl thiolactams 505
- acyl transfer process 124
 - O-centered Lewis base catalysis 511
- α -addition in MBHAD–alkene [3 + 2] annulations, regioselectivity of 767
- alcoholative DKR/KR of α -thioacids 503
- alcohol-based Lewis basic catalysts 511
- alcohol catalysts 511
 - hydroxamic acid based 512
 - acylative amine KR 512
 - phenoxide based 511
 - Steglich rearrangement 511
 - sec-alcohol based 511
 - alcoholative KR of α -substituted ester KR 511
- alcohol dehydrogenases 391, 392, 393
- alcohols 528, 536, 424, 425, 437, 577
 - to ketenes mediated by chiral-planar heterocycles 531
 - Lewis base complex 530
 - peptide-catalyzed kinetic resolution (KR) 1260
- alcoholysis 528, 529, 1326
 - of ketene 536
- aldehyde 534, 538, 540, 544, 548, 554, 557, 743, 1078, 1324
 - addition of silyl ketene acetals 1053
 - addition reactions 1278
 - allylation 282, 1023, 1025
 - amination 1082
 - annulation 744
 - bis- and tris-*N*-oxides 1018
 - bulky 329
 - enamine-mediated enantioselective α -chlorination 882
 - enantioselective allylation 1014, 1125
 - Lewis base-catalyzed allylation 1014
 - and Michael acceptors
 - intermolecular reaction of 1310
 - NHC-catalyzed
 - homoenolate annulation 1332
 - oxidation 1314
 - trifluoromethylation 1316
 - propargylation/allenylation of 1031, 1032
 - reductive amination 1078
 - silylcyanation of 1217, 1220
 - synthetic potential 1079
- aldehyde-ketone cross-benzoin reactions 1302, 1303
- aldimines
 - allylation 1031
 - derivatives, alkynylation of 1032
- aldol addition reaction 155, 164, 209, 210, 223, 294, 303, 311, 317, 321, 324, 325, 327, 328, 330, 743, 876, 877, 1040, 1044, 1045, 1052, 1057, 1058
 - of bridged ketones 908
 - cyclic enol ethers 313
 - cyclohexanone- and propiophenone-derived trichlorosilyl enol ethers 295
 - cyclohexanone-derived trichlorosilyl enol ether 296
 - effect of solvent on 308
 - with enol azolium intermediates 1330
 - enol ethers
 - derived from chiral ethyl ketones 326
 - derived from chiral methyl ketones 321
 - lactate-derived enol ethers 331
 - methyl ketone-derived enol ethers 306
 - nucleophiles 1054

- phosphine oxides 1057
- spectroscopic and mechanistic investigations 1049
- trichlorosilyl enol ethers
 - catalyzed by phosphoramidate 297
 - derived from 326
- aldolization process 295, 302, 304, 309, 310, 311, 312, 1051
- aldol-lactonization process 539, 540, 543, 544, 548, 554, 555
 - cascades of ammonium enolates leading to β -lactones synthesis 538
 - of enolates 561
- aliphatic homoallylic alcohols
 - Claisen rearrangement 1027
- aliphatic β -substituted enals 832
- aliphatic α,β -unsaturated aldehyde 1028
- alkaloid catalysts 529, 540
 - acyl halide-aldehyde cyclocondensations (AAC) 545
 - dimerization 550
 - Nelson's applications of 546
- alkaloid nucleophiles 459
- alkene [3 + 2] annulations 765
- alkene-containing isosteric catalyst 483
- alkene isostere 483
- alkenes 400, 543, 724, 746, 794
 - catalytic, enantioselective, intramolecular, selenoamidation 1170
 - catalyzed enantioselective selenobenzoylation 1169
 - dihydroxylation of 1047
 - diverse sulfenofunctionalization 1171
 - double-bond geometry 1056
 - enantioselective functionalization 1160
 - enantioselective sulfenofunctionalizations reactions
 - by using chiral selenides or substrates 1156
 - enantioselective sulfenofunctionalizations
 - by use of chiral substrates/stoichiometric reagents 1171
 - sulfenofunctionalizations 1156, 1163
 - sulfenofunctionalization reactions 1171
 - by using BINAM-derived phosphoramidate catalysts 1185
- alkoxide 194, 196, 199, 227, 390
 - catalyzed anionic metalate 241
 - catalyzed borosilyl additions
 - to aryl olefins 995
 - catalyzed directed diboron addition 985
 - protonation by MeOH 227
- alkoxyborane 439, 440
- α -alkoxyvinyl silyl hydrides 938
- α -alkyl
 - Calter's lanthanide-promoted ACC 548
- α -alkylallenoates 734, 737
- α -alkyl amino acid scaffold 1086
- α -alkyl aryl acetate esters 474
- alkylation 183, 247, 250, 251, 348, 445, 885
- α -alkylation, of enamines 885
 - photoredox catalysis/enamine-mediated catalysis 886
- S_N1 reactions 886
- S_N2 reactions 885
- α -alkylation product 888
- alkylboronates, synthesis from
 - tosylhydrazones 990
- 2-alkyl-2,3-butadienoates 734, 737
- 2-alkyl dihydropyrroles 728, 756, 780
 - derivatives 757
- alkylidenecyanoacetate substrate 784
- alkylidene β -lactone 550
 - 4-alkylidene β -lactones 553
- alkylidene malonates 1310
- alkyl 6-oxohexa-2,4-dienoates 729
- alkylsulfonate salts, from sulfite alkylations 13
- alkyl trifluoromethylsulfonates 933
- alkyne–ketone [3 + 2] reaction, proposed
 - mechanism of 732
- alkynes 744, 757, 773
 - annulation of 732, 744
- alkyne-to-diene isomerization 790
- alkynoates 725
- alkynylated products
 - fluoride catalysis 261
- alkynylation 261
- alkynyl benzaldehydes
 - trifluoromethylation–cyclization 252
- alkynylmagnesium bromide 261
- allene–aldehyde annulations 741, 771
- allene–alkene and allene–imine [3 + 2] annulations 730
- allene–alkene [4 + 2] annulations, 737, 784
 - synthesis of functionalized cyclohexenes using 739
 - Wang's calculated energy levels of the 738
- allene–alkene [3 + 2] annulations 727, 775, 776, 777, 792, 796
- allene–alkene cyclization 767
- allene double-Michael annulation 752
- allene–imine [3 + 2] annulation 727, 728, 756, 767, 768, 779, 785, 797, 798
- allene–imine [4 + 2] annulation 734, 737, 739, 798, 799
 - mechanistic hypothesis for 734

- allene–imine [3 + 2] reactions 729
- allenes 730
- RC reaction of
 - – with maleimides 703
- allenic esters
- cycloadditions of 1280
- allenoates 734, 752, 755, 758, 776, 1279, 1280, 1283
- derived zwitterionic dienolate 727
- allenones 757
- allylation/propargylation 260
- allyl trichlorosilane 1031
- allylation 255, 260, 281, 286, 292, 1041
- aldehydes 282
 - with allylSi(OMe)₃ 1015
 - competing processes 1015
 - copper(I) fluoride-catalyzed 1242
- allyl azomethine ylide
- [2,3]-rearrangement of 944
- allylic alkylation reactions, asymmetric 425
- allylic trichlorosilanes 281, 283, 284
- allylic trifluorosilanes 282
- allylphosphonium ion 758
- allylsilanes 250, 255, 284, 1020, 1028
- allylsilatranes 260
- allyltributylstannane 1041
- allyltrichlorosilanes 281, 282, 285, 291, 292, 293, 1018, 1026, 1027
- allyltrihalosilanes 1015
- alpine-borane 388, 393, 403
- alstilobanine A and E 562
- ambident nucleophiles 233
- ambidoselectivity 305
- amidation reactions 1314
- amides 470, 552, 1016
- hydrolysis of 688
- amide substrates, N–H acidities 141
- amidine-derived Lewis base catalysts 499
- amidine-ferrocene hybrid Lewis base
- Fc-PIP 585
- β -amido enones 1098, 1099
- α -amido sulfones 583
- α -amination reaction 186
- amine-catalyzed decarboxylations 18
- amine hydrochloride salt 1322
- amine-*N*-oxides 298, 333
- amine oxides 251
- amines 390, 424, 528, 536, 758, 1101
- activation of anhydrides 20
 - based catalysts 10, 494
 - – acylative alcohol/diol KR/
desymmetrization 466, 481, 491, 499
 - – acylative amine KR 475, 486, 505
 - – alcoholative sulfinyl chloride DKR/
sulfonylative diol desymmetrization 489
 - – meso-anhydride alcoholative
desymmetrization ring opening 494
 - – phosphorylative diol
desymmetrization 486
 - – pyrrole/4-dialkylaminopyridine based 464
 - – silylative alcohol KR/diol
desymmetrization 489, 505
 - – Steglich, O \rightarrow C acyl rearrangements 471,
502
 - phosphine, and thiol Lewis basic catalysts in
the intramolecular RC reaction 700
- amino acid-derived phosphinothioureas 700
- α -amino acids 762
- derivatives, enantioselective synthesis 1097,
1098
- β -amino acids 495, 1098
- derivatives, enantioselective synthesis of 566
- α -aminoacrylates 761–763
- β -amino alcohols 495
- in diethylzinc addition 345
- 1,2-amino alcohols 469
- α -amino alkylsilanes
- to aldehydes 939
- amino- and hydroxochroman derivatives,
preparation of 773
- amino-BINOL catalyst 674
- 9-amino(9-deoxy)epi cinchona alkaloids 813,
844, 848
- 3-amino-2,3-dihydrobenzofurans 773
- proposed mechanism for the formation 774
- β -amino ester 572
- synthesis via *in situ* ring opening 572
- (*R*)- γ -amino- β -hydrobutyric acid
(GABOB) 542
- 2-amino-2'-hydroxy-1,1'-binaphthyl
(NOBIN) 481
- aminoindanol-derived triazolium
precatalyst 1302
- α -/ β -aminomalonates 620
- β -amino nitroolefins 1099
- enantioselective reduction 1099
- ammonia, oxidation of
- Oswald's process for 7
- ammonium alkoxide 532
- ammonium dienolates 641, 645
- [4 + 2] cycloaddition of 641
 - α -functionalization 645, 646
 - hetero-cycloadditions of 641
- ammonium enolates 527, 528, 544, 548, 550,
553, 554, 555, 557, 560, 588
- oxyanion 561

- precursors 584
- ammonium phenoxides 251, 261
 - catalyzed reaction 262
- ammonium ylides 604, 611
- amphidinolactone A synthesis 1250
- amplification, of chirality 346
- Armstrong's coupling, of *in situ*-generated ketene and glyoxylate 543
- anhydride ring-opening desymmetrization 498
- anhydrides 460
 - *meso*-anhydrides 494, 495
 - desymmetrization of 494
 - desymmetrization reactions 496
 - as (DHQD)₂AQN 498
 - Lewis base-catalyzed mechanisms 496
 - by methanol
 - transition state model for the desymmetrization 499
- anhydrous fluoride 236
- anilide allenoates 1284
- anionic activators 282
- anionic alkoxy oxygen atom 199
- anionic nucleophile 746
- anion relay chemistry (ARC) 954
- anion stabilizing group 233
- annulations 645, 727, 734, 744, 752, 770, 1331
 - [3+2] annulation 765, 496
 - [4+2] annulation 798
 - of activated alkenes/alkynes and salicylaldehydes/imines 770
- anti*-aldol products 317, 320, 1049
- antibonding orbitals 40, 1039
- anti*-diastereomers 312, 315, 316, 321, 586, 588, 1014, 1047, 1049, 1058, 1059, 1062
- anti*-diastereoselectivity 295, 321, 873, 1046
- anti*-dihydropyranones 588, 589, 590, 591, 592
- anti*-dihydropyridones 593
- anti*-enamine rotamer 167
- anti*-homoallylic alcohol 282
- anti*-isomer 1015
- anti*- β -lactam synthesis 569
 - Fu's catalytic enantioselective 570
- anti*-Mannich reaction 877
- antimitotic agent FR182 877 synthesis
 - via transannular RC reaction 705
- anti*-selective catalyst
 - in Mannich reaction 183
- anti*-selective glycolate aldol reactions 1047, 1048
 - with aldehydes 1048
- anti*-selective pathway 313, 321, 573, 1047, 1060
- syn*- and *anti*-2-silyl-1,3-dithiaanes 945
- 1,5-*anti*-stereoiduction 331
- Arbusov-like transformation 835
- N*-arenesulfonylammonium salts 1266
- aromatic aldehydes 210, 329, 333, 547
- aromatic dipronucleophiles 750
- aromaticity
 - restoration of 579
- N*-aryl- α -aryl glycine derivatives 591
- 2-arylacetic anhydrides 572, 573
- aryl/alkyldenemalononitriles 767
- aryl alkyl ketenes 452, 536, 547, 569, 574
- β -aryl allenoates 757
- N*-aryl-*N*-aroyldiazenes 591
- 3-arylbenzofuranones 472
- 3-arylbenzofurans 473
- 1-aryl-3,3-diisopropyltriazenes 932
- aryl glycines 423
 - derivatives 424
- arylidene arylketones 776, 777
- arylidencyanoacetates 784
- arylidemalonate 734
- arylidemalononitriles 784
 - substrates 794
- N*-aryl imines
 - allylation of 1031
- aryl iodides
 - alkoxide-promoted conversion of 989
- β -aryloxy acid chlorides 548
- α -aryl- α -oxy-silanes
 - intramolecular aldol reaction of 936
- 5-arylproline 1105
- 2-arylpropionic acid derivatives (2-APAs) 527
- 2-arylpropionic esters 528
- 6-aryl-2-pyranones 743
- aryl ring
 - face-to-face π - π interactions of 500
- aryl-substituted benzaldimines 727
- aryl-substituted Boc-imines
 - *in situ* in the presence of CsF 997
- aryl-substituted electrophiles 975
- aryl-substituted ketene imines 1054
- arylthio-substituted silanes 249
- N*-aryl/*N*-tosyl imines 672
- aryl trichloromethyl carbinols 424
- aryl trifluoromethyl ketones 730, 739
- ATPH [Al tris(2,6-diphenylphenoxide)], 931
- π - π attractive interactions 819
- autoracemization 4
- axially chiral biscarboline *N,N'*-dioxides 1022
- axially chiral sesquiterpenes 433
- (2-azaallyl) anion, cycloaddition of 959
- (2-azaallyl)stannanes 959
- azaferrocenes complexes 465

- 1-aza[6]helicene N-oxides
 – scalable route 1130
 5-azaindoline-based catalysts 480, 481
 aza- β -lactams 574
 aza-Michael addition 527, 730
 aza-Morita–Baylis–Hillman (MBH) reaction 195, 212, 213, 215, 216, 223, 224, 665, 1316
 – of activated aryl imines 670
 – adduct 203
 – conversion curves of tosylimine 205
 – general view on traditional and bimolecular mechanism of 213
 – intermediates 225
 – intramolecular 193
 – kinetics 204
 – mechanism 203
 – based on interception 225
 – onychine leveraging 687
 – phosphine-catalyzed 1271
 – photoisomerization reaction
 – proposed transition state for Brønsted acid-assisted proton transfer in 205
 – relationship between relative initial rates and protic additive pK_a for 204
 – of tosyl aldimines 683
 azide-catalyzed reactions 268, 269
 α -azido aryl ketones 421
 α -azido ketone 543
 α -azidomethyl 421
 aziridines 419
 aziridinomitosane 484
 α,β -aziridinyl aldehydes 514
 azodicarboxylates 574
 – C–N bond formation 574
 azolium precatalysts
 – pK_a values 1293
 azomethine arylimines 732
 azomethine imine–allene [3 + 2]
 annulation 731, 782
 azomethine imines 730, 731, 940
 azomethine ylides 941, 949
- b**
 Baker's yeast reduction 438
 basicity scales 61
 Baylis–Hillman reactions 106, 193
B-chlorodiisopinocampylborane (DIP-Cl) 388
 benzaldehyde oxime and (trimethylsilyl) methyl triflate 942
 benzaldehydes 202, 256, 283, 284, 286, 298, 302, 304, 306, 309, 314, 318, 319, 322, 324, 329, 343, 344, 356, 675, 743, 744, 745, 906, 1079
 – catalyzed by chiral phosphoramides 287
 – electronic properties 1024
 – enantioselective allylation of 1243
 – from propanal 657
 benzaldimines 213, 727, 730, 734
 benzhydrylium ions 93
 – with Lewis bases, reactions of 93
 – reactions of isothiourreas 102
 benzofuran-2-ones 791
 benzoin condensation 1, 8, 9, 12
 benzoin cyclization products 1299
 benzoin reaction 1303
 – NHC-catalyzed 1340
 benzomorphan-based κ -opioid 374
 benzophenone 399, 400
o-benzoquinone diimides 582, 583
 – in formal [4 + 2] cycloadditions 582
o-benzoquinone imides 581, 582
 – in Lewis base catalysis 581
 benzotetramisole (BTM) 500–502, 593, 603
 1,5-benzothiazepines
 – Asano and Matsubara's synthesis of 635
 benzothiazolines 752
 1,3-benzoxathioles 752
 1,4-benzoxazinones 581
 – derived heterocycles 581
 benzoxazolines 752
o-benzoyl derivatives 528
 benzoyl fluoride 616
 benzoyl halides 492
N-benzoyl hydrazones 1030
 – of ethyl glyoxylate 1031
 benzoyl peroxide (BPO) 880
O-benzoylquinine 553, 564, 594, 597
 benzyl/allyl silanes 249
 benzyl anion 253
 – formation 254
 α -benzylation 253, 889
 – of α -aryl-methyl aldehydes 885
 benzyl-2,3-butadienoates 735, 739, 777
 benzyl conformation, x-ray evidence 820
 benzylic alcohols
 – with ketenes and diketenes 465
N-benzylidene aniline 610
 2-benzylxyacetaldehyde 548
 benzyloxycarbonyl (CBz)-protected γ -aminoalkenes 1189
 benzylsilanes
 – Pd-catalyzed coupling 254
 – stereospecific fluorodesilylation–alkylation of 254
 benzyl sodium anion 245
 1-benzylsulfenyl-1,2,4-triazole 884

- benzyltrimethylammonium fluoride (BTAF) 907
- Berzelius definition of catalysis 3
- BF₃ affinity scale 61, 75
- BF₃–Lewis base 75
- BH₃ complex 397
- BH₃–DMS reduction 399, 406, 411, 415
- BH₃/THF reduction 400
- BH₃–1,4-thioxane 395
- bicyclic benzoyl ammonium intermediate salt 492
- bicyclic-β-lactone 555, 557, 623
- bicyclic NHC catalyst 1300
- bicyclic P-chiral phosphines 781
- bidentate amines 270
- bidentate DPPP catalyst 790
- bidentate Lewis acid 548
- bidentate phosphine catalyst 777
- bifunctional amidine catalyst 1197
- bifunctional catalysis 204, 271, 340, 548, 1217, 1253
- chiral catalyst 777
 - *in situ* generation 1223
 - mechanism 1225
 - proposed catalytic cycle 567
- bifunctional cocatalytic enantioselective β-lactam 568
- bifunctional 3,3'-diphosphoryl-BINOLate-Zn (II) catalysts 357
- bifunctional Lewis base-Lewis acid catalysis 6, 339, 340
- Bigeleisen–Mayer equation 394
- BINAM (1,1'-binaphthalene-2,2'-diamine)
- backbone 1181
 - derived thiophosphoramides 1167
- binaphthol aluminum triflate complex 568
- binaphthylphosphine 791
- BINAPO 333, 1057, 1062
- axially chiral diphosphine oxides 1020
 - -catalyzed aldol addition 333
 - – of trichlorosilyl enol ether 334
 - -catalyzed direct aldol addition 333
 - dihedral angle 1021
 - direct aldol addition catalyzed 334
 - double aldol addition of 2-butanone catalyzed 335
 - Lewis base catalyst 1128, 1135
 - *meso*-epoxide opening 1129
- BINOL 204
- -containing Lewis acids 677
 - -derivative 678
 - -derived bifunctional phosphine catalyst 702
 - -derived phosphoric acid 1018
 - moiety 356
 - -phosphoric acid catalyst 1190
- (*R*)-BINOL ligand 676
- biomimetic aldol-lactonization process 562
- bipyridine mono-*N*-oxides 1022
- bipyridine-*N,N'*-dioxide 1137
- biquinoline *N,N'*-dioxide 1032
- Birman's catalyst 501, 502
- second-generation catalyst structures 500
- 1,3-bis-(2,6-diisopropylphenyl)imidazolidinium (SIPr) 1297
- 1,3-bis(diphenylphosphino)propane (DPPP) 750, 752
- bishomoallylic alcohols 986
- bis-methoxyboron derivative 983
- bis-*N*-oxide bipyridines
- library synthesis
 - – terpenes derived 1127
- bis-*N*-oxide-catalyzed aldol addition of trichlorosilyl enol ethers 333
- bis-*N*-oxide-catalyzed reaction 333
- bis(phenols)
- peptide-catalyzed desymmetrization 1261
- (*R,R*)-4 bisphosphoramide 1042
- bisphosphoramide catalysts, design and optimization of 286
- bisphosphoramides 287, 1051, 1052
- application in synthesis 1029
 - SnCl₄ complexes 289
- 2,2'-bispyrrolidine 286, 287
- bisquinolyl-bis-*N*-oxide 270
- bis-sulfinamides 1031
- bis-sulfinimide 1092
- bis-sulfonamide 224
- bis-tetrahydroisoquinoline *N,N'*-dioxide 1022
- 3,5-bis(trifluoromethyl)benzoyl functionality in catalyst 784
- 3,5-bistrifluoromethylbenzylamide group 786
- 2,6-bis(trifluoromethyl)phenyl seleniranium ions 1165
- bis(tris(trimethylsilyl)methyl)zinc
- X-ray analysis of 341
- boat-like structure
- transition structures 313, 314, 317, 321, 328, 416
- Boc-imines 1284, 1327
- N*-Boc phenylglycine
- (*L*)-enantiomer of 848
- Boc-protected amide 141
- bond energy 394
- ω-bonding 51
- bond order 394
- bond strength 400

- borane-dimethyl sulfide 441
borane complexation 388, 390, 397, 417, 419, 434, 436, 441
borane-diethyl aniline (BDEA) 441, 445, 452
borane-dimethyl sulfide 432, 441, 444, 447, 450, 451
borane-THF 434, 439, 450
boron-substituted quaternary carbons 971
Borrmann–Wegler methodology 539
 β -boryl aldehydes 975
 β -boryl carbonyls 974
 β -boryl carboxaldehydes 971
 β -borylcyclohexane
– at ambient temperature 971
 β -boryl, β -hydroxy ketone 972
 β -boryl ketones 978
boryl/silyl conjugate additions
– enantioselectivity of 1003
 β -branched acid chlorides 544
 α -branched alkyl aldehydes 677
(\pm)-bremazocine 374
Breslow intermediates 18, 19, 971, 1295, 1300, 1308, 1314, 1322
– benzimidazolium based 1296
– riazolium-based aza-, 1296
– TEMPO oxidation 1324
Bürgi–Dunitz trajectory 498
bridged ketones, aldol reaction of 908
Brønsted acid (o-FC₆H₅CO₂H) 141, 216, 392, 532, 656, 678, 858, 975, 1013, 1081, 1097, 1162, 1165, 1168
– acidic cocatalyst 862, 891
– acidic functional group 864
– catalyzed enantioselective MBH reaction 678
– catalyzed MBH reactions of cyclohexenone catalyzed by thioureas 679
– cocatalyst on enantioselectivity 845
– cycle 537
– definition 35
– mediated sulfenofunctionalization conditions 1189
– trifluoromethanesulfonimide (Tf₂NH) 843
Brønsted affinity scale 63
Brønsted base 129, 265, 554, 555, 630, 693, 728, 745, 746, 747, 770, 788
– amines, basicity of 1189
– assisted phosphine catalysis 763
– catalyzed pathway 537, 1297
– mediated proton transfer mechanism 786
Brønsted equation 91
Brønsted–Lowry definition 38
 α -bromination 597, 599, 883
– processes 599
bromoaminocyclization 1202
– using aminothiocarbamate catalyst 1203
bromocyclization 1190
 α -bromocyclohexylcarbaldehyde 508
bromodichloromethylsilanes
– fluorodesilylation of 251
bromoetherification, mechanism of 1205
bromohydrins 1027, 1115
bromolactonization
– bifunctional amidine catalyst 1199
– by using cinchona-derived amino thiocarbamate 1198
 α -bromomethylacrylates 766
2-bromopropionyl bromide 550
Brønsted acid 223
– trifluoromethanesulfonimide (Tf₂NH) 843
Brook rearrangement 954
1,2 Brook rearrangement 662
(–)-brucine 459, 538
 β -substituted cyclopentenones
– enantioselective NHC-catalyzed boryl conjugate additions 980
2,3-butadienoates 724, 727, 730, 752, 756, 772
tert-butane sulfinyl chloride
– DKR of 490
2-butanone 333
2-butenylsilanes 282, 283
(*E*)-/*(Z)*-2-butenylsilanes 283
n-butyl addition 309
– to acetophenone 373
butyl groups (*trans*-1-butyl-2,3-dipropylseleniranium hexafluoroantimonate) 1163
n-butyllithium, alkylation 445
1-*N*-butyl-3-methylimidazolium 219
 γ -butyrolactones 545
O-Bz quinidine 534
- C**
C(2)-acylammonium salt
– X-ray crystal structure of 609
C-acylation 475
– of mixtures of (*E*)- and (*Z*)-acyclic silyl ketene acetals 476
– of silyl ketene imines 477
C-2 acyl triazolium salts 508
Calter's ketene dimerization method 552, 553
Calter's lanthanide-catalyzed AAC 549
C(1)-ammonium enolates 527, 579, 584, 592, 593, 600
C(2)-ammonium enolates 527, 604

- C(3)-ammonium enolates 527
 camphor-derived NHC catalyst 1302
 carbamates 536, 537
 – Fu's enantioselective synthesis 536
 – -modified promoters 699
 carbanion 265, 954
 – equivalents 936, 960
 – – with Si-C-EWG 906
 – – silicate dichotomy 252
 – transfer reactions
 – – catalytic cycles 235
 – trapping reactions 936
 carbanion generation
 – alkylation of 947
 – from Si-C-C 914
 carbanion transfer reactions 265
 carbene catalyst 1308, 1324
 carbene formation 251
 carbene-mediated organocatalysis 1291
 carbenes, metal complexes of 1291
 carbocycles formation
 – via homoenolate equivalents 1334
 carbohydrates 484
 carbon basicity 91
 carbon–carbon bonds 150, 1044
 – formation 149, 151, 152, 153, 154, 295, 305, 306, 339, 909
 carbon-13 isotope effects 398, 399
 carbon Lewis basicity 85
 carbon nucleophiles 245
 – triorganosilyl-mediated transfers of 233
 carbon nucleoside 436, 437
 – analogs 436
 – precursor 437
 carbonyl carbons 399, 732
 – electrophilicity 1013
 carbonyls 433, 437, 759
 – aldol-type reaction of 1057
 – containing substrate 387
 – electrophile 235
 – enamines-promoted enantioselective α -oxidation of 880
 – oxygen atom 732
 – silylcyanation 1232
 carbonyl ylide
 – 1,3-dipolar cycloaddition 937
 carbosulfonylation 1186, 1187
 – reaction time course
 – – effect of additives and catalyst on 1189
 carboxylic acid 554, 555, 557, 584, 588, 591, 779, 800, 957
 carboxylic acid-derived C(1)-ammonium enolates 588
 – in Michael addition processes 584
 Carreira's catalytic system 1251
 catalysts
 – regeneration 390, 391
 – resting state 537
 – structure, and variation 124–130
 – turnover 1242
 catalytic
 – activities 347
 – amination 536
 – hydrogenation 423
 – Lewis base 237
 – reactions 393
 – restoration by fluorotriethoxysilane 1239
 – transformation 141
 catalytic amination 536
 catalytic asymmetric organozinc addition reaction
 – advances in catalytic enantioselective organozinc addition to aldehydes 353
 – catalytic enantioselective
 – – addition of Grignard reagents 367
 – – organozinc addition to ketones 358
 – organozinc reagents/titanium isopropoxide 350
 – scope of carbonyl substrates 350
 catalytic asymmetric zinc-free alkynyl addition 367
 catalytic CBS reduction 390
 catalytic α -chlorination using C(1)-ammonium enolates 596
 catalytic cycle 389, 573, 575, 590
 – proposed for MBH reaction 223
 catalytic cyclopropanation 606
 catalytic efficiency 549
 catalytic enantioselective 996
 – alkynylzinc addition to aldehydes 355
 – arylzinc addition
 – – to ketones 364
 – carbosulfonylation
 – – scope of 1185
 – dialkylzinc addition
 – – to simple ketones 362
 – diethylzinc addition 354
 – – to benzaldehyde 344
 – – to α -keto esters 361
 – dimethylzinc addition
 – – to α -keto esters 361
 – ethyl addition to benzaldehyde 346
 – organozinc addition to aldehydes 344
 – phenylzinc addition clemastine synthesis 363
 – reactions 393

- sulfenoamination 1190
- sulfenoetherification
 - Lewis bases survey 1177
 - scope of 1178
- sulfenofunctionalizations 1177
- catalytic power 387
- in yeast alcohol dehydrogenase 392
- catalytic tetra(p-chlorophenyl)porphyrin iron chloride 612
- catalytic Zn(II) ate reagents 377
- catecholates 242, 282
- catecholborane 390, 397, 401, 410, 416, 423, 429, 431, 433, 436, 444
- cation affinity numbers 59
- cationic arylselenium complex 1168
- cationic hexacoordinate complex 1016
- cationic phosphonium species 786
- cationic silicon assemblies
 - penta- and hexacoordinate 284
- cation- π interactions 388
- C(1)-azolium enolates 584
- C–B bonds
 - enantioselective methods 967
 - formation 971, 983
- CBS catalyst 389
- CBS-mediated kinetic resolution 433
- CBS reduction 388, 390, 391, 392, 395, 396, 407, 409
 - alpha;-acetals 419
 - acetyl η^5 -cyclopentadienyl rhenium 425
 - allenyl ketones 423
 - alpha;-azido ketones 421
 - beta;-dialkyl nitro ketones 422
 - 1,3-diketones 431
 - establish key stereocenter in a total synthesis of estrone methyl ether 430
 - [5]ferrocenophane-2-one 426
 - ketone 441, 443
 - β -keto sulfides 420
 - in organic synthesis 416
 - O-THP ketones 418
 - prochiral diketone selectively 438
 - pro-chiral 1,3-diketones to 1,3-bis-alcohols 438
 - racemic diketone 439
 - racemic monocarbonyl substrates 432
 - racemic spiroketone 439
 - synthesis of silane diol serine protease inhibitor 447
 - transition state 407
 - trichloromethyl ketones 422
 - unstable atropisomers 433
- centrosymmetric reduction substrate 432
- cesium trifluoromethyl sulfinate 935
- CF₃
 - anion 252
 - CF₃-PIP 500
 - group 252
 - Lewis Base-Induced Transfer 921
- CFCM solvation model for CH₂Cl₂ 1183
- CF₃SiMe₃ 921
 - amides and lactams 928
 - aminoketones 923
 - carbonyl compounds 922, 925
 - carboxylic acid halides 927
 - cyclic anhydrides 927
 - esters and lactones 926
 - oxazolidin-5-ones 927
 - ylation, vinylation, and alkylation 932
- chain-carrying species 237
- chair-like transition state models 315, 1059
- chair-like transition structure 301, 318, 319, 320, 326, 328, 333, 412, 1049
- chalcogen elements 73
- chalcone derivatives
 - NHC-catalyzed carboannulation 1334
 - predominantly produces (Z)-trichlorosilyl enol ethers
 - *in situ* conjugate reduction 1061
- chalcone-derived azadiene 1337
- chalcone, formation of 907
- charge–dipole interaction 61
- charge localization 396
- CH₃/CD₃ isotope effect 407
- chelatable Lewis base 339
- chelation 322, 328
- chemical bond
 - Lewis definitions of 34
 - rule of two 34
- chemo- and enantioselectivity of reduction 430
- chemo-, regio-, or stereoselective organocatalysis 141
- ChiPros® 460
- chiral acyl ammonium/pyridinium salts 477
- chiral acyl azides 536
- chiral acyl-transfer reagent 1324
- chiral alcohols 530
 - kinetic resolution (KR) 1322
 - stereocenters 417
- chiral aldehydes 312
- chiral alkyl(diphenyl)phosphine 699
- chiral allylic phosphonium species 792
- chiral amino alcohol 340
- chiral β -amino carbonyl compounds 877
- chiral aminophosphine 784

- chiral ammonium enolate 528
 chiral 2-aryl-2-phosphabicyclo[3.3.0]octanes (PBOs) 459
 chiral 2-arylpropionic acid 527
 chiral azolium salt precatalysts 508
 chiral bifunctional catalysts 204
 chiral bifunctional phosphine promoters 675
 chiral biheteroaromatic diphosphine ligands 1130
 chiral binaphthyl catalysts, as phosphine promoters 672
 chiral binaphthylphosphine 791
 chiral BINOL-Li(I)-catalyzed enantioselective alkynylation 367
 chiral BINOL-Ti(IV)-catalyzed enantioselective alkynylation 366
 chiral bis-oxazolidinone 957
 chiral bisoxazoline, magnesium complex of 271
 chiral Brønsted acid 532, 537
 – counterion 530
 – cycle 537
 – pathway 536
 chiral γ -butenolides 791
 chiral bypyridine-*N*-monoxides
 – mechanism of allylation catalyzed 1023
 chiral α -carbonyl quaternary center 1028
 chiral catalysts 536, 537
 – based on cinchona alkaloids 291
 – for enantioselective allylation 1016
 – – aromatic and aliphatic *N*-oxides as catalysts 1021
 – – phosphoramides/phosphinoxides as catalysts 1017
 chiral 3,3'-dialkoxyphenyl-BINOLs 352
 chiral 4-dialkylaminopyridines 464
 chiral diamino-salen ligand 361
 chiral dihydropyrroles 780
 chiral dinuclear Ti(IV) catalyst 352
 chiral dipeptide phosphine 779, 786, 798
 chiral dipronucleophiles 750
 chiral 3,3-disubstituted oxindoles 786
 chiral 4-DMAP
 – catalyst 466, 467, 469
 – Fu's quadrant-based design strategy 466
 – organocatalysts 471
 chiral DMF analogs 1083
 chiral enamines 107
 – -mediated processes 894
 chiral endo-phosphine 782
 chiral ferrocenyl 4-PPY-based catalyst 477
 chiral(*o*-hydroxyaryl)phosphoramidate 355
 chiral β -hydroxyesters 540
 chiral isothiurea catalyst 504
 chiral β -lactams 579, 796
 chiral β -lactones 795
 chiral Lewis base-promoted net [2 + 2] cycloaddition 547
 chiral Lewis bases 281, 282, 283, 291, 538, 544, 549, 1040, 1050, 1054
 – activation technology 1066
 – catalysts 1016, 1160
 chiral *N,O*-ligands
 – proposed Zn(II)/Ti(IV)-dinuclear intermediates 351
 chiral *O,O*-ligands 355
 chiral, methylene-linked bisphosphoramides 287
 chiral mono-thiourea-based HB donor catalyst 481
 chiral *N*-acyl aminophosphine 778, 784
 chiral α -oxygenated carbonyl compounds 880
 chiral α -oxygenated ketones 881
 chiral phosphabicyclo[2.2.1]heptane 775
 chiral phosphines 774, 779, 786, 794, 795
 – catalysis 462, 774
 – oxides 1016, 1057
 – promoter 675
 chiral phosphonamides 1018
 chiral phosphonium dienolate 775
 chiral phosphoramidate 294, 311, 312
 – allylation reactions 283
 – catalyst 331
 chiral (*o*-hydroxyaryl)phosphoramidate-catalyzed enantioselective diethylzinc addition 355
 chiral phosphoramides 281, 283, 287, 298, 314, 322, 749
 chiral phosphoric acid (*R*)-TRIP 845
 chiral 4-PPY
 – stoichiometric quantity of 478
 chiral 4-PPY-based catalyst 474
 chiral pyridine-*N*-oxides 286
 – mechanism of allylation catalyzed 1024
 chiral pyridine-*N*-oxides, allylation catalyzed 1024
 chiral pyrrole-based catalysts 464, 466
 chiral selenides 1159
 chiral selenium derivatives
 – empirical optimization 1157
 chiral selenium electrophiles 1159
 chiral α -silyl ketones 534
 chiral spirophepene 782, 790
 chiral γ -substituted acrylates synthesis, using chiral phosphabicyclo[2.2.1]heptane 787
 chiral γ -substituted crotonates 788

- chiral sulfoxides 1016
- chiral β -sultams 578, 579
- chiral synthon
 - preparation 417
- chiral TADDOLate-Ti(IV) 367
- chiral tertiary alcohols 358
- chiral tetrahydrofurans/tetrahydropyrans
 - synthesis, using chiral spirophosphine 790
- chiral tetrahydropyrazolopyrazolone 782
- chiral thiazolium-based catalysts 1291
- chiral thiourea anion binding agents 480
- chiral thioureaphosphine 793
- chiral triazolium salt 508
- chiral trichlorosilyl enol ethers 321, 331
- chiral trifluoromethylated compounds 924
- chiral trityl pyrrolidine 881
- chiral Zn(II)-salen complexes 365
- chloral-derived imine 578
- o*-chloranil 580
 - in formal [4 + 2] cycloadditions 580
- chlorinated β -lactones 543
- α -chlorination 594, 599
 - of acid chlorides 594
 - of aldehydes 881
 - using column asymmetric catalysis 597
- α -chloroamines
 - synthesis of 1096
- chlorodiphenylphosphine 425
- chloro epoxide 543
 - kinetic resolution 1134
 - – reaction condition optimization, for 1134
- α -chloro esters 599
- chloroform 205, 207, 432, 741
- chloroformates 472
 - activator 1227
- chlorohydrin synthesis
 - from cis-alkenes
- α -chloro imines 1095
- α -chloro ketones
 - reductive amination 1095
- chlorolactonization, with (DHQD)₂PHAL 1196
- chloromethyl crotyl silanes 257
- chloromethyl trimethylsilylmethyl sulfide, with dipolarophiles 949
- α -chlorosilyl ether 291, 301, 310, 317
- N*-chlorosuccinimide (NCS) 881
- chlorosulfonylation 1172
- p*-chlorotosylimine 205, 206
- α -chloro trichlorosilyl ethers 310
- chymotrypsin 446
- cinchona 494, 497
 - alkaloid catalysts 498, 540, 543, 552, 553, 563, 583
 - cinchona alkaloids 495, 924
 - catalyzed formal [4 + 2] cycloadditions 584
 - natural/unnatural compounds 495
 - cinchona-based primary amines 872
 - cinchona-catalyzed epoxidations 845
 - cinchonidine 494
 - cinchonine 494
 - cinnabaramide A 562
 - cinnamaldehyde 808, 1062
 - derived-iminium salt 817, 819
 - electrophilicity parameters 808
 - NHC-catalyzed carboannulation 1334
 - *N*-cinnamyl ammonium salt 943
 - cinnamyltrimethylsilane 256
 - CIP
 - C–Li or C–Na bonds 245
 - lithium reagent 249
 - (*R*)-citronellic acid 554
 - ¹³C KIE evaluation of transition states 227
 - ¹³C KIE modeling 152
 - Claisen condensation 550
 - Claisen-like rearrangement 1338
 - Claisen's crossed aldol condensation 4
 - click chemistry 394
 - Cl₃SiH 1079
 - aldehydes and primary amines 1081
 - benzaldehydes and butylamine 1080
 - enantioselective reduction of imines 1104
 - reductive amination of aldehydes 1079
 - – and primary 1080
 - reductive amination of functionalized aldehydes 1080
 - by TMEDA, reductive amination of 1082
 - *epi*-C₉ O-acetylquinidine 555
 - coal gasification 7
 - cocatalysts 221, 581
 - proline 216
 - thiourea 215, 216
 - cocatalytic kinetic resolution 1144
 - Co(III)-Lewis base bifunctional catalyst 549
 - Co(III)-salen complexes 549
 - collisional activation theory 7
 - colored EDA complex
 - light irradiation of 890
 - complex molecular constructs 724
 - computational chemistry 74, 210, 409
 - cone angle 72
 - conformational distortion 393
 - conformational equilibrium
 - constant 407
 - conformationally flexible catalyst 415

- conformational rigidity on diastereoselectivity, effect of 1158
- Conia-Ene reaction 1313
- conjugated enamides
- enantioselective reduction 1098
- π - π Conjugate/ π - σ^* hyperconjugate conformations in *o*-phosphoryl Zn(II)-phenoxides 357
- contact ion pairs (CIP) 245
- cooperative LA/LB system 581
- coordinate covalency 34
- copolymers 540
- Corey–Bakshi–Shibata (CBS) reduction 387
- Corey–Link reaction 423, 424
- Coulombic interactions 741
- covalent catalysis 387
- C-protonation 1322
- C-pyramidal nucleophilic intermediate 937
- Cr(CO)₃-complexed meso-1,4-diol 493
- cross-aza-benzoin reaction 1305, 1306
- of aliphatic aldehydes 1305
 - – and Boc-imines 1306
 - with trifluoromethyl-ketimines 1306
- cross-benzoin oxy-Cope sequence to cyclopentenes 1305
- cross-benzoin reactions 1299, 1302, 1303, 1304
- with aldehydes and ketones 1303
 - enzymatic 1301
 - using aliphatic-aromatic aldehydes 1301
- crossed-aldol reactions 301
- of aldehydes 1044
- cross-metathesis 586
- crotonaldehyde 323, 324
- conjugate addition of water 806
- crotylation
- copper(I) fluoride catalysis 1242
- E*-/*Z*-crotyltrichlorosilanes 1026
- 18-crown-6 ether (18-C-6) 914
- CsF-induced desilylation of sulfonium salt 951
- σ_{C-Si}
- hyperconjugative interaction of 110
- C–Si bond 238
- formation with chiral NHCs 993
- C-silylated benzyloxymethyl cyclopentanone 936
- C₂-symmetrical pyrrolidine derivative 1088
- C₂-symmetric bidentate chiral phosphines 775
- C₁-symmetric carbene 977
- C₂-symmetric chiral N,N,O,O-ligand 359
- C₂ symmetric phosphoramides 283
- Cu-catalyzed enantioselective additions 975
- Curtin–Hammett principle 822
- cyanation 264, 1231
- cyanide-catalyzed benzoin formation 1297
- cyanide ion
- amine-catalyzed addition 265
 - in cyanation reactions 267
- cyanide nucleophilic species 268
- α -cyano acetates 749
- cianoaminosilanes
- cycloaddition of 941
- 2-(4-cyanobenzyl)-2,3-butadienoate 735
- α -cyano esters 759, 760
- α -cyano ketones 760
- α -cyano menthyl esters 749
- α -cyanomethylaminosilanes 941
- cyanopyrrole 536
- 2-cyanopyrrole 535, 536, 537, 538
- Fu's catalytic enantioselective addition 535
- cyano-silylation of aldehydes 1315
- α -cyanosulfones 756
- cyclic carbamates
- amidine and isothiourea-catalyzed KR 506
- cyclic (\pm)-1,2-monobenzoyle-cis-diols 468
- cyclic 1,2-monoprotected diols 468
- cyclic sulfonamides 578
- cyclic trichlorosilyl enol ethers 313
- cyclic voltammetry 1296
- cyclizations 727, 731, 741, 744, 760, 773, 779
- reactions of alkenes 773
 - to six-membered analog 697
- cycloaddition 547, 890
- alkylidene azomethine ylide 943
 - [2+2] cycloaddition 539
 - – of ketene and chloral 540, 561
 - – to form β -lactams 563
 - [3+2] cycloaddition/esterification
 - – mechanistic pathways of 615
 - [4+2]-cycloaddition 581, 639, 640
 - – with chloral, Peters' ammonium dienolates 638
 - – with diene, iminium ion 806
 - *in situ*-generated ketene 548
 - pathway 721, 775
 - products 805
- cycloalkanone-derived enol ethers 317, 320
- cycloalkanone-derived trichlorosilyl enol ethers 313, 320
- cyclobutadiene iron tricarbonyl complex 425
- cycloheptanone-derived enol ethers 316
- cyclohexane carboxaldehyde 314, 1042, 1043
- (*R,R*)-*trans*-1,2-cyclohexanediamine 283
- cyclohexanone
- enolate 1338
 - to nitroalkenes

- enamine-catalyzed Michael addition of 869
 - (*R*)-cyclohexene 699
 - meso*-1,4-cyclohexyl-dione
 - desymmetrization 429
 - 1-cyclohexyl-2-phenylthio-1-heptanone 419
 - cycloisomerization 697
 - cyclopentadiene 429
 - Diels–Alder reaction of 806
 - η^5 -cyclopentadienyl rhenium (I)
 - derivative 424
 - cyclopentadienyl ring 424
 - cis*-2-cyclopentene-1,4-diol 492
 - cyclopentenones 554, 721, 724, 727, 730, 759, 760, 765, 767, 775, 776, 778, 779, 782
 - formation mechanism 1334
 - formation through tandem γ -umpolung– β' -umpolung annulation 761
 - synthesis 724
 - through MBHAD–alkene [3 + 2] annulation, preparation of 768
 - cyclopentenones 214
 - tri-*n*-butylphosphine- promoted reaction of 676
 - cyclopropanations 604
 - cyclopropanes 440, 608
 - carboxylates, aldol reaction 912
 - formation 605
 - cyclopropenyl silane
 - protodesilylation regiochemistry of 258
 - cycloreversion 194
 - cyclothiazomycin 441, 442
 - cysteine-derivative
 - intramolecular RC reaction 701
 - cysteine-derived catalysts 699
- d**
- DABCO 558
 - catalyst 657
 - equilibrium constants 106
 - DABCO-catalyzed RC-type step 706
 - DABCO-catalyzed reaction 200
 - methyl acrylate 677
 - DABCO-mediated RC dimerization 689
 - of acrylates 690
 - (–)-DAIB
 - four-center and six-center transition states 349
 - mechanism of 349
 - proposed catalytic cycles 348
 - DAIB system 349
 - enantioselectivity-determining transition structure 349
 - Zn(II) five-membered rings 347
 - Dakin–West reaction 1, 24, 25
 - Deng's DHQD-PHN catalyst 499
 - density functional theory (DFT) 48, 74, 154, 178, 208, 223, 394, 409, 497, 721, 722, 727, 816
 - calculations 208, 833, 971, 988, 1043
 - of transition states 1183
 - total energy 209
 - deoxy-Breslow intermediate 1318, 1319
 - imidazolylidene-derived 1319
 - deoxygenation of polyols 486
 - deprotonation 536, 578, 747, 752, 754, 766, 792, 1062
 - of dinucleophile 752
 - desilylation-aldol reaction
 - of ketone 908
 - desilylation, with TASF 240
 - desolvation 387
 - desymmetrizations 432, 434, 460, 1229
 - bromoetherification using catalyst 1205
 - CBS reduction and retro-Diels–Alder reaction 430
 - of *meso*-aziridines 1229
 - of *meso*-dicarbonyl substrates 426
 - of *meso*-diols 491, 492
 - of tert-alcohols 489
 - deuterium 404, 722, 730, 735
 - atoms 762
 - isotope effects 402, 735
 - KIEs at homotopic positions 408
 - labeling of $S_{N2'}$ – $S_{N2'}$ cascade mechanism, evidence from 764
 - steric KIEs 415
 - deuterium labeling, in support of α -umpolung addition mechanism, evidence from 762
 - N,N*-dialkylbenzylammonium *N*-methylide
 - Sommelet-Hauser and Stevens rearrangement 944
 - N,N*-dialkyl-2-methylbenzylamine 944
 - α -dialkyl α -nitro ketones 421
 - dialkylsubstituted ketenes 547
 - dialkylzinc (R_2Zn) 343
 - via Schlenk equilibrium 368
 - meso*-diamines
 - desymmetrization of 480
 - 1,2-diaryl-1,2-diaminoethanes 480
 - diarylketone products 1314
 - diarylprolinol 409
 - ether-derived iminium salts 835
 - silyl ether 892
 - silyl ether catalysts 152, 858, 863
 - diarylthiourea 222
 - N,N*-diarylthiourea 222

- 3,4-diaryl-*trans*- β -lactams 572
- diastereoselection 312, 320, 321, 329, 331, 439, 995
- aminolysis of ketenes 535
 - aziridination
 - – Yadav's catalytic 610
 - external 331
 - formation of amide 535
 - methods 545
 - NCAL processes 557, 561
 - protonation 531
 - sulfenofunctionalization 1172
- diastereospecific lithiation 424
- diastereotopic CF₃ groups
- DNMR studies 243
- diastereotopic silyl halides
- fluoride-induced intramolecular alkylation 254
- diazabicyclo[4.3.0]non-5-ene] (DBN) 1143
- 1,4-diazabicyclo[2.2.2]octane (DABCO) 99, 486, 551
- 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) 975
- diazomethane anions 233
- dibenzoyl tartaric acid (DBT) 1133
- diboron additions
- to alkenes and alkynes 985
 - effectively 986
- diboron reagent 989
- diborylation
- syn-selectivities 986
- β -dicarbonyl compounds 754
- dicarbonyl reductions 437
- 1,3-dicarbonyls 1303
- substrate 429
- dichlorinated aldehydes 540, 542
- dichlorination with (DHQ)₂PHAL
- representative scope of 1206
- dichotomy of α - and β -functionalization of acrylates 1318
- 1,8-di(dimethylamino)naphthalene 1097
- Diels–Alder lactonization (DAL) 628, 629
- Diels–Alder–Rauhut–Currier reaction
- enzymatic 704
- Diels–Alder reactions 429, 632, 810, 813, 823, 825, 826
- to acrolein with α -alkyl substituents 843
 - amine-catalyzed 814
 - of cinnamaldehyde 814
 - cycloadditions 822–825
 - with first-generation MacMillan catalyst 824
 - with methacrolein 843
 - preorganized cation- π system 827
- 2,4-dienals
- trienamine-mediated enantioselective Diels–Alder reaction of 894
- diene–alkene [3 + 2] annulation, rationale for 729
- dienoates
- acceptors 1309
 - vinylogous aza-MBH reaction of 684
- dienolate 779, 780, 781, 783, 784
- azolium, annulation of 1339
- dienol ethers 1068
- dienones
- RC–Wittig reaction of 692
 - vinylogous aza-MBH reaction of 684
- dienoxysilane nucleophile 1248
- dienylsulfones 683
- β -diesters 756
- 4-(diethylamino)pyridine-based chiral catalyst 481
- diethyl azodicarboxylate 892
- diethyl phosphonate 445
- diethyl 2-vinylidenesuccinate 741, 783
- diethylzinc addition 343, 346, 365
- to aldehydes 343
 - to benzaldehyde 345
 - Lewis basic activation of 353
- (difluoroallyl)silanes 256
- 3,5-difluorobenzoyl group 784
- α,α -difluoro ester 913
- dihydrobenzofuran carboxylates 584, 585, 586
- 2,3-dihydrobenzofurans 771, 772
- 1,4- and 2,4-dihydrobenzooxazines 750
- 2,3-dihydrobenzimidazoles 750
- dihydrocoumarin derivatives synthesis 725
- dihydrofurans 730
- and piperazines, synthesis of 757
 - synthesis, through allene–ketone [3 + 2] annulation 731
 - Tang's synthesis 612
- 2,3-dihydroindoles 750, 790
- dihydropiperidinones synthesis 1337
- dihydropyranones 618
- products 590
- dihydro-2-pyranones 741, 742, 743
- 3,4-dihydropyrans 696
- dihydropyridazinones
- synthetic applications 642
- dihydropyridones
- synthetic applications of 644
 - Ye's net [4 + 2] synthesis of 644
- dihydropyrroles 727–730, 767, 768, 779–782, 798
- formations 780

- intermediate 798
- through diene–alkene [3 + 2] annulation 730
- 2,3-dihydropyrrrolopyridines 750
- dihydroquinidines DHQDs
 - four low-energy conformations of 497
- dihydroquinine-2,5-diphenyl-4,6-pyrimidinediyl diether 577
- diiodine affinity scale 60
- trans*-2,5-diisopropylpyrrolidine 958
- 1,3-diketone 438
 - Michael donors 617
- diketones 440
 - proline-catalyzed Robinson annulation of 857
- 1,4-diketones 440
- meso*-diketone substrate 429
- dilithium salt of BINOL 1105
- dimeric catalyst survey 1140
- dimeric chiral Ti(IV) complex 352
- dimeric cinchona alkaloid-based catalysts DHQD₂(AQN) 495
- dimeric DAIB-Zn(II) catalysts 351
- dimeric organozinc species 345
 - amplification of chirality 346
 - catalyst efficiency 345
 - reaction pathway and transition states 348
- dimeric phosphoramides 302
 - catalyst 1050
- dimethyl acetylenedicarboxylate (DMAD) 732, 744
- 4-(dimethylamino)pyridine (4-DMAP) 121, 531, 551
 - “super”-nucleophilic behavior of 459
- dimethylformamide (DMF) 130, 283, 1077, 1078, 1079
- trans*-3,4-dimethyl-4-(3-hydroxyphenyl)-piperidine core 445
- 1,3-dimethyl-2-imidazolidinone (DMI) 692
- 2',5'-dimethylisobutyrophenone 406
- dimethyl *N*-acryloylpyrrolidine-2,5-dicarboxylate 1172
- dimethylphenylphosphine 770
- dimethyl-2-silyl-1,3-dithianes 946
- dimethyl sulfoxide (DMSO) 141
- 2,4-dinitrobenzoic acid (DNBA) salt 829
- dinuclear BINOLate-Zn(II) structure 352
- meso*-diol 492
 - 1,3-diol motif 438
 - 1,2-diols 469
 - derivatives 486
 - cis*-1,2-diols 489
 - derivative 487
 - desymmetrization of 489
 - KR and desymmetrization of 491
- meso*-1,2-diols 469
- meso*-1,4-diols 492
- dioxane 741
 - 1,3-dioxane
 - derivative 1101
 - scaffold 1090
 - 1,4-dioxane 342, 368
- dioxanes 741, 742
- dioxanone 198, 200, 224, 227
 - pathway 224
- N,N'*-dioxide 1027, 1029
 - application in synthesis 1029
- 1,3-dioxygenated motifs 545
- (*R,R*)-DIPAMP 777
- DIP-Cl reductions 400, 402, 403
- DIP-Cl transition state 400
- diphenylchlorophosphate (DPCP) 1262
- 1,1-diphenylethanol 130
 - PPY-catalyzed acetylation of 130
- 1,1-diphenylethylene 251
- diphenylphosphine 425
- diphenylphosphinoylimines 779–781
- diphenylphosphinyl group 778, 779
- N,N'*-diphenylphosphoramide 314
- diphenylprolinol silyl ether aminocatalysts 893
- diphenylprolinol silyl ether-derived enamine 862
- diphenyl[(trimethylsilyl)methyl]sulfonium triflate 950
- diphenylzinc 363
- diphosphate (ThDP)-dependent enzymatic catalysts 1300
- 1,5-dipolar cyclization reaction 946
- 1,3-dipolar cycloaddition 937, 939, 949, 958
- dipolarophiles 616, 727, 728, 741, 770
 - activating group 725
- dipole–dipole interactions 61, 205
- dipole–dipole repulsion model 544
- dipronucleophiles 750, 752, 757, 759, 760, 770
- dipropionate synthon
 - enantioselective synthesis 551
- di-*p*-toluyltartaric acid 444
- diquinanes 724, 767
 - derivatives 724
 - syntheses 725
 - synthesis 725
 - and tetrahydrocyclopenta[c]furans, synthesis of 768
- direct aldol reaction
 - diastereo- and enantioselectivity 1060
- direct enol azolium precursors 1338

- β,β -disubstituted acyclic enones 977
 γ -disubstituted allyltrichlorosilane 1028
 α,α -disubstituted ammonium enolates 544, 547
 2,6-disubstituted aryl electrophiles for catalytic enantioselective sulfenoetherification 1183
 3,3'-disubstituted cyclopentenes 767
 β,β -disubstituted enals
 – enantioselective transfer hydrogenation 840
 2,3-disubstituted indoles 1102
 α,α -disubstituted β -lactones 547
 α,α -disubstituted- β -lactones synthesis 547
 β,β' -disubstituted unsaturated carbonyl compounds 983
 3,3-disubstituted phthalide moiety 791
 α -disulfones 756
 1,3-di-*t*-butyl-imidazolium 1295
 2,6-di-*tert*-butylpyridinium triflate salt 531
 1,3-dithianes, carbanions derived 944
 2-dithianyl and 2-methyl-2-dithianyl 238
 dithianyl systems 248
 DMAP (4-dimethylaminopyridine) 561, 1263
 – based catalyst 466, 474, 544
 – Boc₂O method for the Boc-protection of cyclic amides 140
 – catalyzed N-acylation 481
 – nucleophilicity of 100
 DMAP-benzhydrylium adduct 100
 DMAP-catalyzed acetylation 136, 137
 – of alcohols 131, 132
 – of carbohydrates 137
 – consensus mechanism for 122
 – of cyclohexanol 132
 – of propan-1-ol and propan-2-ol 131
 – of selected alcohols with acetic anhydride 137
 DMAP-catalyzed isobutyrylation 131
 – of menthol 131
 DMAP-catalyzed reaction 123
 – of acetic anhydride 123
 – of Boc₂O 139, 140
 – vs. uncatalyzed reaction rates for acylation of cyclohexanol 133
 DMAP-functionalized styrene 130
 DMAP-mediated reaction
 – of Boc₂O 140
 – of N-nucleophiles with Boc₂O 140
 DMF-promoted addition of allyltrichlorosilanes 283
 DMPU 1161
 DMSO 792
 – pK_a values 249
 – – water 263
 D-myo-inositol-1-phosphate (D-I-1-P) 1262
 D-myo-inositol-3-phosphate (D-I-3-P) 1262
 donor/acceptor
 – bond energy 62
 – interactions 33
 – – in quantum mechanical symbols 38
 – Robinson's classification of 36
 donor number (DN) 59
 double-aldol additions 1064, 1065
 – using different phosphine oxides 1065
 double desilylation, of disilylmethyl amine 943
 double diastereoselectivity 545
 double-Michael, addition to activated alkynes/allenes 750
 double-Michael annulations 752
 [D₃]-1,1,3,3-tetramethylcyclohexane 407
 dual-activation
 – allyl transfer 259
 – catalysis 1215
 – by Lewis base
 – – proposed catalytic cycle 1141
 – mechanism 350
 dual catalysis 548
 Dunitz pyramidalization 108
 dynamic kinetic resolution (DKR) 433, 434, 466
 – of a rapidly equilibrating mixture of diastereomers via CBS reduction and conversion 435
 dyotropic process 561
- e**
 E/C character of affinity (enthalpy) scales 61
 Edwards parameters 86
E-enol 301, 304
 – ethers 303, 317, 320
 effective partial pressure 56
 π electron capacity (π acidity) 104
 electron-deficient ketimines 668
 electron-deficient olefins 873
 electron density
 – donor 55
 – source 55
 electron-donating bis-cyclohexyl imidazolium salt 971
 σ electron-donor 104
 electron donor ligand Me₃SiCH₂ 382
 electronegative substituents
 – apicophilicity of 50
 electron localization function (ELF) 1314
 electron pair acceptors (EPA) 55, 76
 electron pair donor (EPD)
 – EPA interaction 75
 – EPA molecule 55

- electrophile–nucleophile combinations 110
- electron-poor
 - aromatic aldehydes 1045, 1070
 - aryl groups 618
 - carbonyl compounds 554
 - iminium cation 816
 - para-substituted aldehydes 675
 - substituents 743
- electron-rich
 - aldehydes 547, 1044, 1058
 - aromatic aldehydes 1054, 1056
 - aryl groups 618
 - bisphosphine oxide 1058
 - electron-poor aryl groups 612
 - and electron-poor benzaldehydes 1047
 - heteroaromatics 825
 - phosphine oxide 1065
- electron-withdrawing 1044
 - aryl trifluoromethyl ketones 365
 - effect 726
 - substituents 234
 - – conversion of ketones 1097
- electrophiles 233, 689, 721, 726, 729, 730, 746
 - aldehydes 538, 542
 - carbonyl compounds 554
 - imino ester 564, 566
 - ketone 558
 - –nucleophile combinations
 - – second-order rate constants for 90
 - –nucleophile systems 770
 - reactivity of iminium ions 807
 - through electrostatic interactions 864
- electrophilic selenenylation 1156
- electrophilic sulfonylation
 - of alkenes 1170
- electrospray ionization, coupled to mass spectrometry 195, 217
- electrostatic bonds 61
- electrostatic complementarity 392
- electrostatic interaction 732
- electrostatic stabilization 155, 588
- electrostatic-to-covalent (E/C) bonding ratios 61
- electrovalency
 - for transfer of electron 34
- β -elimination 706, 825
- enal redox pathway
 - mechanism of 1325
- enals
 - [3+2] cycloaddition of 817
 - enantioselective α -fluorination 1330
 - NHC-catalyzed homoenolate annulation 1332
 - NHC-catalyzed β -hydroxylation 1328
 - NHC-catalyzed oxidative esterification 1342
 - phospho-Michael reaction of 833
 - primary amine-catalyzed enantioselective epoxidation 846
- enamine-mediated catalysis 864, 888, 892, 895
 - acidic cocatalyst 862
 - applications 892
 - – vinylogy 892
 - π conjugation of 862
 - enamine nitrogen, pyramidalization 859
 - HOMO-raising activating effect 859
 - imidazolidinone catalysts 866
 - mechanistic considerations 859
 - -mediated stereoselective transformations 893
 - primary vs. secondary amines 860, 861
 - prolinol-derived catalysts 864
 - reactivity 859, 862
 - stereoselectivity 863
 - steric control approach 864
 - in total synthesis 893
 - transition metal catalysis 895
- enamine-mediated enantioselective
 - intramolecular [6 + 2] cycloaddition 891
 - inverse-electron-demand hetero-Diels–Alder reaction 891
 - S_N1 -type alkylation of aldehydes 887
 - syn-Michael addition 872
- enamine-mediated Michael addition
 - to nitro-olefins 875
 - to nitro-olefins catalyzed 875
- enamines 110, 150, 153, 825, 863
 - activation processes
 - – electrophiles suitable 112
 - –aldol reaction catalyzed by the imidazolidinone 866
 - α -alkylation
 - – photo-organocatalytic enantioselective alkylation 889
 - -based enantioselective transformations 863
 - -based mechanism 149
 - catalysis 881
 - and diastereo-divergent dual-catalysis 896
 - enantiofacial discrimination 864
 - imine tautomeric equilibrium 1102
 - intermediates
 - – *in situ* detection and structural characterization 152
 - mechanism 150
 - -mediated aminocatalysis 884
 - -mediated transformations 864
 - nucleophilicity 109, 878
 - – parameters 111

- oxazolidine equilibrium
- - in diphenylprolinol 865
- -promoted aldol mechanism 680
- -promoted enantioselective α -amination of carbonyl compounds 879
- -promoted enantioselective α -chlorination of aldehydes 881, 882
- -promoted enantioselective α -fluorination of aldehydes 883
- *in situ* NMR studies 152
- enantio-/diastereoselective synthesis, of ring B via CBS reduction application 448
- enantiodivergent phosphorylation 1262
- enantioenriched
 - *N*-acylpyridinium salt 602
 - 2-azido-1-ethanols 421
 - cyclopentenes 775
 - enone 797
 - fluorohydrins 1144
 - product 1160
 - seleniranium ion 1160
 - thiiranium ions 1173
- enantioenriched seleniranium ions
 - configurational stability 1163
 - generation and capture of 1165
 - pathways for racemization 1163
- enantiomerically enriched thiiranium ions
 - nucleophilic opening 1175
- enantioselection 201, 281, 283, 289, 292, 298, 302, 304, 305, 308, 309, 311, 316–318, 333, 387, 393, 395, 422, 437, 531, 537, 539, 542, 543, 551, 556, 557, 560, 572, 588, 589, 776, 779, 780, 783, 784, 788, 791–793, 1016, 1018, 1052, 1064, 1072
 - acylations 459, 460, 774
 - - of secondary alcohols 774
 - addition of achiral amines to ketenes 535
 - alcoholysis of ketenes 532
 - aldol addition
 - - of trichlorosilyl enol ether catalyzed by chiral phosphine oxide 334
 - - of trichlorosilyl ketene acetal 294
 - alkene functionalizations
 - - Lewis base-catalyzed 1155
 - alkylation 349, 353
 - α -alkylation of aldehydes 888
 - alkynylation
 - - of ketones 364, 365
 - allene–alkene [3 + 2] annulation 775
 - allene–alkene [4 + 2] annulation 784
 - allene–imine [4 + 2] annulation 783
 - allene–imine [3 + 2] annulations 781
 - allylations 281, 289, 292, 1015, 1016, 1239
 - - construction of quaternary centers by 289
 - - silver(I)-catalyzed 1238, 1240
 - - silver(I) fluoride-catalyzed 1239
 - - synthesis of serotonin antagonists by 293
 - allylations of carbonyl compounds 1017
 - allylic substitution 791
 - aminocatalysis 868
 - annulation 779, 780
 - [2 + 2] annulations 795
 - [3 + 2] annulations 775, 787, 792
 - [4 + 2] annulations 782
 - aza-MBH applications 668
 - aza-MBH reactions 671, 674, 677
 - azomethine imine–allene [3 + 2] annulation 782
 - benzoin reactions 1298, 1299
 - Brønsted base-assisted [3 + 2] annulation 792
 - α -bromination 599
 - bromoetherification, under cooperative catalysis 1204
 - catalysis 774
 - C–B bond formation 983
 - conversion of ketenes to esters 532
 - cyanations
 - - with binaphthol catalysts 272
 - - with catalyst 271
 - - with oxazolines 272
 - - with salen complex 273
 - cycloaddition reactions 890
 - [4 + 2] cycloadditions of C (1)-ammonium enolates 579
 - Diels–Alder reaction 822
 - dienolate addition
 - - copper-catalyzed 1246
 - diethylzinc addition 354, 359
 - dihydropyrrole formation 779
 - 1,3-dipolar cycloaddition 615
 - with DMAP derivatives 531
 - enamine-based transformations of aldehydes 867
 - exo-Diels–Alder reaction 839
 - α -fluorination 883
 - - of C(1)-ammonium enolates 599
 - - trifunctional catalytic system 602
 - formal [2 + 2] and [3 + 2] cycloadditions 573
 - formal [4 + 2] cycloadditions 579
 - of the formamide catalysts 1091
 - α -functionalization of aldehydes 858
 - glycolate aldol addition 1047
 - hydrogenations 387, 774, 787
 - - catalysts 387
 - intramolecular MBH reaction 675

- intramolecular γ -umpolung addition 790
- inverse-electron-demand hetero-Diels–Alder reaction 890
- ketoketene–imine [2 + 2] annulation 796
- β -lactam synthesis
 - – bifunctional catalytic system 567
 - Lewis acid-catalyzed MBH reaction 676
 - MacMillan catalysts/geometry control
 - – Diels–Alder reaction 822
 - – first- and second-generation 814
 - – Friedel–Crafts reaction with electron-rich aromatics 825
 - – Mukaiyama–Michael reactions with enolsilanes/silylated nucleophiles 829
 - Mannich–Lactamization cascades 562
 - Michael addition 786
 - – lactonization 584
 - – promoted by Fc-PIP 585
 - Michael–aldol– β -lactonization (NCMAL) 624
 - Mukaiyama–Michael reaction of silyloxyfurans 831
 - NCAL process with ketoacid substrates 560
 - nucleophile-catalyzed acyl transfer 459
 - organocatalytic triple cascade 874
 - oxazaborolidine-catalyzed deacylation, of meso-*N,N*-diacetyl imidazolones 427
 - oxazaborolidine-catalyzed reduction, of carbonyl compounds 441
 - Passerini-type reaction 1072, 1073
 - phosphine catalysis 774, 791
 - phosphorylation of enals 834
 - α -protonation
 - – of ketenes 527
 - RC reaction, of symmetrical bis-enones promoted 701
 - reduction 1095
 - – of an acetyl cyclobutadienyl iron tricarbonyl complex 426
 - – of α -azido ketones 421
 - reduction of imines 1087, 1088
 - – formamides derived from proline and pipercolic acids 1084
 - – pyridine- and imidazole-derived catalysts 1089
 - – sulfinimide- and phosphoramidate-type catalysts 1091
 - route to biotin employing oxazaborolidine-catalyzed desymmetrization 429
 - selenofunctionalization 1161
 - silyl conjugate additions 995
 - silylcyanation 1232
 - sulfenofunctionalizations 1173
 - sulfenylation
 - – of alkenes 1173
 - synthesis 446
 - – of α -amino acids 423
 - – of frondosin B 450
 - – of functionalized acrylates 791
 - total synthesis of (+)-ibophyllidine 798
 - γ -umpolung 787
 - version, of Kwon's [4 + 2] annulation 783, 784
 - Weitz–Scheffer-type epoxidation reactions, of α,β -unsaturated aldehydes 845
 - [2Y+Y2], 1338
- enantioselective cyanosilylations 270
- enantioselective [3+ 2] cycloaddition
 - catalyzed by D-Thr-L-*t*-Leu-derived catalyst 1281
- enantioselective epoxide opening 1122
 - Lewis acid-catalyzed 1115
- enantioselective α -fluorination 1331
- enantioselective formation
 - of C–Si bonds 967
- enantioselective halofunctionalization 1192, 1194, 1195
 - mechanistic considerations 1192
- enantioselective hydration 1330
- enantioselective phosphitylation 1264
- enantioselective α -protonation 1330
- enantioselective selenoetherification
 - catalytic mechanism 1168
 - morpholine-derived thiophosphoramidate catalyzed 1167
- enantioselective selenofunctionalization 1166
 - Lewis base-catalyzed 1157
- enantioselective sulfoetherification
 - catalytic mechanism 1181
 - with chiral Brønsted acid 1179
- enantioselective sulfenylation 1266
 - phosphoric acid catalyzed 1191
- endocyclic amido group
 - electron-withdrawing inductive effect 863
- 5-endo cyclization 756
- energy surface diagram for Lu's [3 + 2] annulation 723
- enolates 537, 568
 - alkylation 447
 - condensation 12
 - O-alkylation of 859
- enol ethers 301, 302, 309, 323, 331, 333, 1059
- conformation 323
- geometry dependence of the aldol additions 302
- enol lactonization 612

- enones 746
 - -acids 585
 - -acid starting materials 585, 586
 - Basavaiah's RC dimerizations of 690
 - β -carbon 697
 - enantiopure acid cocatalyst and solvent on the epoxidation 847
 - Lewis base-catalyzed β -functionalization of 86
 - MBH reaction 657
 - primary amine-catalyzed enantioselective epoxidation 846
 - pyrrolidine-catalyzed addition 811
 - RC reaction and cyclization of 696
 - enoxy silane derivate 1062
 - enriched γ -substituted allyltrichlorosilanes 1025
 - enthalpy 56, 57, 58, 59, 62, 392
 - (affinity) vs. Gibbs energy (basicity) 61
 - scales 56
 - enzyme-catalyzed reactions 391
 - epoxide opening
 - achiral Lewis bases catalyzed 1116
 - with bipyridine-*N,N'*-dioxide
 - proposed catalytic cycle 1137
 - with ferrocenediylazaphosphinine-catalyzed TMSCl 1120
 - HMPA-catalyzed
 - electronic effect, role of 1122
 - steric effects, role of 1122
 - HPMA-promoted 1123
 - with Lewis base-catalyzed chlorotrimethylsilane (TMSCl) 1116
 - with Lewis base-catalyzed organotin halides 1122
 - meso*-epoxide opening
 - di-*N*-oxide bipyridines catalyzed 1127
 - with HMPA catalyzed SiCl₄, 1121
 - mono-*N*-oxide bipyridines catalyzed 1127
 - epoxides
 - alkylations 238
 - cooperative Lewis acid/Lewis base catalyzed fluorination 1142–1143
 - enantioselective opening of
 - chiral catalysts 1131
 - helical catalysts 1131
 - pyridine *N*-oxide catalysts 1131
 - fluorination of 1142
 - Lewis base-catalyzed kinetic resolution, 1133
 - chlorosulfolipid synthesis, applied to 1135
 - phenyl isocyanate insertion 1122
 - ring opening (*See also* epoxide opening)
 - phosphaferrrocene catalyzed 1119
 - phosphazirrocene catalyzed 1119
 - meso*-epoxides
 - dimeric Lewis base catalyst 1142
 - enantioselective chlorination of 1123
 - enantioselective desymmetrization
 - Lewis bases with unconventional ligand structures catalyzed 1130
 - *N*-oxide-derived Lewis bases catalyzed 1123
 - phosphine oxide Lewis bases catalyzed 1128
 - phosphoramidate Lewis bases catalyzed 1123
 - enantioselective desymmetrization of 1123
 - enantioselective opening
 - with chiral bis-phosphine oxide-catalyzed SiCl₄ 1129
 - with fluoride 1144
 - enantioselective opening of
 - SiCl₄ 1121, 1124
 - kinetic resolution
 - by enantioselective fluoride addition 1148
 - planar chiral *N*-oxides 1124
 - meso*-epoxides opening
 - allene catalyzed 1132
 - with phosphaferrrocene-catalyzed TMSCl 1117
 - by PINDOX catalyzed SiCl₄ 1126
 - epoxylactones, aldol reaction 912
 - equilibrium isotope effect (EIE) 408
 - erythromycin A 484
 - phosphorylation 1265
 - erythromycin, Woodward synthesis of 806
 - erythronolide B 545
 - ESI(+)-MS plot
 - of aza-MBH reaction 224
 - of MBH reaction cocatalyzed by *N,N'*-diaryl thiourea 222
 - spectra for the MBH reaction of methyl acrylate 219
 - ESI technique 217
 - E*-tetrahydropyrazolopyrazolone 782
 - ethyl allenolate, with exocyclic enones
 - amine-catalyzed RC reaction 694
 - eupolauridine, from onychine 688
 - (–)-3-*exo*-(dimethylamino)isoborneol (DAIB) 344
 - exo*-selective Diels–Alder reaction 841
 - Eyring behavior 393
- f**
- face-to-face π – π stacking 469, 470
 - Fc-PIP-catalyzed Michael addition–lactonization 586

- Felkin–Ahn model 312
 ferrocenophane-2-one substrate 424
 FerroPHANE 776
 Fischer-Tropsch method 7
 fluorescence assay
 – for catalyst screening 483
 fluoride
 – catalysis 237
 – – vs. aldehydes allylation 1236
 fluoride-assisted expulsion
 – thermochemical estimates 246
 fluoride-catalyzed 247
 – allylic isomerization 257
 – carbanion transfers
 – – nucleophiles 234
 – desilylation 905
 fluoride (salen)Co complex 1146
 fluoride-initiated reactions 247
 fluoride ion 237, 260
 – allylation using allylSiMe₃ 1015
 – catalysis 260
 – -catalyzed conditions 256
 – -initiated S_N2 displacement of alkyl halides 246
 – -mediated synthesis 615
 fluoride-promoted
 – addition of allylfluorosilanes to aldehyde 282
 – borosilyl additions to boc-imines 995
 fluorination
 – with NFSI 1330
 α-fluorination
 – trifunctional system 601
 α-fluoro acids 1330
p-fluorobenzyl moiety 1102
 fluorodesilylation 247, 251
 – mechanism of 234
 – technique 263
N-fluorodibenzenesulfonimide (NFSI) 883
 fluorofunctionalization reactions 1192
 2-fluoro-6-methoxyphenol 791
 4-fluorophenyl/4-nitrophenyl silanes 263
 fluorotriethoxysilane 1243
 fluorous tag 1103
 fluorovinyl anions 263
¹⁹F NMR spectroscopy 204
 formal [2 + 2] cycloadditions 564, 565, 568, 569, 574, 576, 577, 578
 – to form β-lactams 565
 – of ketenes and imines 562
N-formyl proline amide 1094
 free energy 210, 212, 227, 392, 393, 537, 722
 – of activation 537
 – difference ΔΔ(G) 538
 Friedel–Crafts acylation 407, 540
 Friedel–Crafts alkylation
 – of *N*-methylpyrrole 817
 – on indoles accepts 828
 – between *N*-methylpyrrole and enals 828
 – to *N*-methylindole and crotonaldehyde 826
 Friedel–Crafts-type reactions 810, 825
 frontier molecular orbital (FMO)
 – superimposition of 860
 frustrated Lewis pairs (FLP) 72
 fugacity coefficient 56
 β-functionalization of acrylates 1318
 α-functionalization of enals 1330
 β-functionalization of enals 1324
 γ-functionalized acrylates synthesis, through phosphine-catalyzed γ-umpolung addition 756
 α-functionalized esters 1330
 furan oxidation 447
 furaquinocin E 194
 Fu's catalyst 480
 – enantioselective
 – – aza(-)lactam synthesis 574
 – – oxazetindin-3-one synthesis 575
 – for KR 467
 fused bicyclic β-lactones
 – Romo's achiral NCMAL 623
 6,6- and 5,6-fused ring systems, synthesis of 744
 fused tricyclic β-lactones
 – dyotropic rearrangement of 562
 Fu's tertiary α-chloroester synthesis 598, 602
- g**
- gas-phase acidity 258
 – –base interactions 58
 gas-phase basicity (GB) 58
 gas-phase fluoride affinity 240
 – silanes bearing increasing numbers of fluorine atoms 240
 gas-phase proton affinities 60
 gauche-open conformation 499
 Gaunt's catalytic intramolecular enantioselective cyclopropanation 609
 gem-trifluoromethyl substituents 242
 geranylgeranyltransferase-1 737
 – inhibitors 728
 Gibbs energy 5, 55, 56, 57, 58, 59, 61, 62, 76
 – scales 56, 62
 Gladiali's phosphopine 776, 783
 α-glucosidase inhibitors 540
 glycolate aldol reaction 1047

- glycolate ethers
 – kinetic enolization of 1047
- glycosidation 797
- glyoxalate hydrazones
 – enantioselective allylation of 1244
- (*S*)-goniothalamine 1029
- Grignard reactions
 – addition reaction 367, 375
- Grignard reagents 261, 340, 367, 368, 369, 372, 373, 374, 376
 – catalytic enantioselective alkyl addition 369, 370
 – RMgCl-derived zinc(II) ate complexes 373
- Grob-type fragmentation 791
- group transfer reactions 1259
- Gutmann acceptor number 205, 207
- Gutmann analysis 46
 – empirical analysis 1040
 – of acid–base interactions 44
 – spillover effect 48
 – principles 47, 1180
 – of molecular adduct formation 46
- h**
- β -hairpin conformations 483, 484
- Hajos–Parish–Eder–Sauer–Wiechert (HPESW) reaction 145
- haliranium ions
 – competitive nucleophilic capture and olefin transfer 1193
 – derived from alkenes of various substitution patterns 1192
 – mechanism of olefin-to-olefin transfer 1192
 – olefins to-olefin transfer 1193
 – racemization
 – by olefin-to-olefin transfer 1192
- meso*-haliranium ions
 – enantioselective opening 1203
- α -haloaldehydes 508
- halo-aldehydes
 – α -alkylation 885
- γ -haloallyltrichlorosilanes
 – to vinyl epoxides synthesis 1027
- halocarbocyclization 1195
- halofunctionalizations 1156
- halogen-substituted phenyl groups 675
- halolactonization 1196
- halomethyl anions 250
- Hammett correlations 206, 268, 273
- Hammett study 268
- Hammond postulate corollary 1052
- hard and soft acids and bases (HSAB) 60
- Hartree–Fock nonlocal exchange 213
- Hauser rearrangement 944
- Hayashi–Jørgensen enamine 111
- Hayashi–Jørgensen-type prolinol ether catalyst 107
- Hayashi–Jørgensen catalyst 862
- H-bonds (HBs) 479
 – acceptors 489
 – donors 470, 1026
- 2H-chromenes 702
 – via enantioselective RC reaction 702
- Heck cyclization 754
- Heck reaction 1318
- Heisenberg uncertainty principle 404
- helical pyridine *N*-oxide 1032
- hemiketal
 – alkoxide intermediate 212
- heptacoordinate silicon 1095
- heteroarylacetic acids 588, 590
- heteroatom-containing dipolarophiles 727
- heteroatomic electrophiles reactions 878
 – α -amination 879, 880
 – α -halogenation 881
 – α -oxidation 880
- α -heteroatomic functionalizations 884
- α -heteroatom-substituted aldehydes 508
- α -heteroatom-substituted carbanion 936
- α -heteroatom tin reagents
 – with alkyl halides 959
 – to carbonyl compounds 958
- heterocycles 538, 574, 578, 727, 741, 752, 757, 770
 – synthesis, through mixed double-Michael additions of allenates 753
- N*-heterocyclic carbene (NHCs). *See* NHCs (N-heterocyclic carbene)
- heterocyclic lactone, [3Y+Y3] cycloaddition with homoenolate 1334
 – enals/aldehydes, [3Y+Y2] annulation of 1332
 – enals/imines, [3Y+Y2] annulations of 1333
 – enals/trifluoromethyl ketones, [4+2] reaction 1339
- hexachlorosilicate dianion 1050
- hexacoordinated
 – complex (SiL₆) 49
 – difluorosilicate 255
 – neutral complex 286
 – phenanthroline spiro complex 243
 – silicates 244, 245, 260, 284
 – silicon species
 – *in situ* formation 1078

- structures 242
 - transition state 256
 - 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) 1143
 - hexamethylphosphoric triamide (HMPA) 283, 1220
 - hexamethylphosphorous triamide (HMPT) 739, 1160
 - 3-hydroxyquinuclidine 202
 - (±)-hirsutene 724, 797, 799
 - Hiyama coupling 938
 - HMPA reaction
 - with SiCl₄, NMR studies on 1139
 - HMPA(Se) 1161
 - as the catalyst 1162
 - -catalyzed selenoetherification 1162
 - HMPA/SiCl₄
 - multinuclear NMR analysis 1050
 - Hünig's base 543, 544, 553, 554, 578, 600
 - for the cycloaddition of *in situ*-generated ketene 543
 - dehydrohalogenation of 599
 - homoaldol-lactonization process 641
 - homobenzotetramisole (HBTM) 501, 558, 616
 - homodimerization 553
 - of ketoketenes 795
 - of methylphenylketene 553
 - homoenolate annulation reactions 1333
 - homoenolate chemistry
 - NHCs (*N*-heterocyclic carbene) catalyzed 1332, 1334
 - homopropargyl hydrazide 1032
 - HOMO-raising activation
 - of enamine-mediated catalysis 892
 - HOMO-raising enamine activation of aldehydes 866
 - Horner-Wadsworth-Emmons reaction 921
 - Hosomi–Sakurai allylation 1237
 - Houk–
 - List-like model 170, 171
 - List-like transition states 178
 - List model 153, 154, 167, 169, 179, 183
 - List transition states 150, 151, 155, 181
 - hydrazones 281
 - propargylation/allenylation of 1031
 - syn*-hydroacylation 1313
 - hydroacylations
 - of enol ethers 1313
 - meso*-hydrobenzoin 508
 - hydroboration 400
 - hydrocinnamaldehyde 309
 - hydrogenation 4, 6, 423, 432, 553, 590
 - with Ru/TsDPEN complex 424
 - hydrogen bond 61, 62, 68, 265, 388, 483, 741, 777, 780, 783, 786, 791, 794
 - donors 741, 777
 - interactions 196
 - hydrogen-bonded intermediate 672
 - hydrogen-bonding thiourea catalyst 702
 - hydrogen cyanide reactions 265
 - hydrogenic wavefunction 404
 - hydrolysis 436, 437, 448
 - of glycosides 3
 - of starch 3
 - 9-*epi* hydroquinidine-derived primary amine catalyst 871
 - hydroquinone (HQ) 881
 - hydroquinuclidine (HQD) 683
 - α-hydroxy alkanooates 501
 - hydroxybenzotriazole (HOBt) 551
 - β-hydroxy benzyl esters 508
 - α-hydroxy carboxylic acid 574
 - γ-hydroxy enones 1067
 - α-hydroxy ester 580
 - β-hydroxy ester 910
 - α-hydroxy ketones
 - primary amine-mediated syn-aldol reaction 876
 - β-hydroxy ketones 746, 1059, 1061
 - δ-hydroxy lactams 1069
 - β-hydroxylation of enals
 - via single-electron oxidation 1329
 - hydroxyl-directed cyclopropanation 440
 - hydroxyl-directed diastereoselective diboron additions
 - to alkenes 987
 - hydroxypyrrone substrate 1338
 - 3-hydroxyquinuclidine 202
 - β-hydroxy sulfides 420
 - ω-hyperbonds by Weinhold and Landis (NBO analysis) 1040
 - hypervalent bonding 49
 - analysis 49
 - hypervalent iodine compound 935
 - hypervalent Si–C bond 244
 - hypervinylogous aldol addition 1070
- i*
- imidate methylide cycloaddition 940
 - imidazole 264, 481
 - catalysis of 4-nitrophenyl acetate hydrolysis 22
 - imidazolidinones 152, 867
 - catalysis 812, 814, 815, 881
 - -derived enamines

- X-ray crystal structures 867
- imidazoliums 1291
 - experimental and computational acidities 1294
 - scaffold 1291
- imine 204, 206, 238, 270, 562, 734, 771, 798, 805
 - approaches, *Si*-face of 877
 - enantioselective reduction 1085, 1087, 1089, 1090
 - nucleophilic attack, preferred directions of 1101
 - propargylation/allenylation of 1031
 - [2 + 2] reaction with 646
 - reduction, attempted rationalization 1094
 - with trichlorosilane, enantioselective reduction 1092
- iminium 150
 - catalysis
 - kinetic studies 808
 - solvent effects 813, 814
 - cations 805
 - hydrolysis 175
 - intermediates 832, 1078
 - ions
 - electrophilic reactivities 111
 - salts
 - dipolar cycloaddition 942
 - optimized geometries and relative energies 818
 - X-ray structure 821
- iminium catalyst. 806, 812, 813 *See also* iminium catalysis
- iminium-catalyzed
 - cycloadditions 806
 - Diels–Alder reactions 810, 823
 - saturation kinetics 809
 - Friedel–Crafts reaction 826
 - structural and mechanistic aspects 806
 - of α,β -unsaturated aldehydes 806
- iminium–cyclopentadiene Diels–Alder reactions 825
- indane-derived amino alcohol 450
- indan-1-ol
 - silylative KR 507
- indene carboxylates 584, 585
- indole 849
 - enantioselective reduction 1102
 - to enones, enantioselective conjugate addition 849
 - Friedel–Crafts alkylation of 847
 - N–H moiety of 850
- TS optimized structures 851
- indole-3-carboxaldimine 798
- indolines
 - acylative KR of 479
 - enantioselective reduction 1103
- 2-indolyldihydropyrrole 798
- In(III)-complexed cinchona alkaloid derivative 567
- meso*-inositol derivatives 486
- inositol polyphosphates 486
- in situ* borane and oxazaborolidine catalyst formation 452
- in situ* dehydrative generation 363
- in situ*-generated ketenes 551, 566
 - Armstrong’s cycloaddition of 544
 - Calter’s ketene dimerization 552
 - dimerization 553
- in situ*-generated α,β -unsaturated acylammonium 628
- in situ* preparation
 - of alkenylzinc species 360
 - of borane–diethylaniline complex 451
- π – π interaction 1046
- n – π^* interactions 85
- intermediate nitrilium ion
 - hydrolysis 1165
- intermediate phosphonium salt 792
- intermolecular
 - aldol-lactonizations 554
 - aldol reaction 540, 544
 - [4 + 2] cycloadditions 588
 - KIEs as a mechanistic tool, limitations of 400
 - net cycloadditions of ketenes 544
- intramolecular
 - aldehyde allylation 257
 - allene–alkene [3 + 2] annulation 797
 - [3 + 2] annulations 724, 767, 797
 - coordination 440
 - cyclization 578, 584, 765, 772
 - KIEs 398
 - at homotopic groups 400
 - Michael addition 757
 - NCAL reaction 554, 558
 - nonbonding interaction dictates 1159
 - nucleophile 14
 - proton transfer 737
 - Rauhut–Currier/aldol reaction 743, 744
 - reactions using chiral selenium electrophiles 1159
 - selenoetherification 1159
 - selenofunctionalizations 1159
 - substrate-controlled transfer 437
 - transesterification 200

- β' -umpolung addition 760
 - γ -umpolung addition 790
 - γ -umpolung reaction 756
 - intramolecular 1,2-shift 235
 - inverse temperature dependence
 - for stoichiometric reduction of acetophenone 395
 - iodide-assisted hydrolysis 14
 - iodocarbocyclization
 - stereochemical models 1195
 - iodolactonization
 - via anion binding/Lewis base coactivation 1200
 - isothiourea 558, 570
 - structures 101
 - tetramisole 588
 - isothiourea-mediated α -amination
 - of carboxylic acids 594
 - isothiourea-mediated Michael addition–lactamization 595
 - isothioureas 102, 588
 - nucleofugalities 104
 - -type catalyst 502
 - -type Lewis base catalysts 502
 - isotopically labeled silyl-substituted triphenylcyclopropene
 - desilylation of 258
 - Itsuno/Corey ligands and CBS catalysts 389
- j**
- Jacobsen's chiral thiourea phosphine catalyst 793
 - Jensen's classification, of donor–acceptor interactions 40
 - Jørgensen-Hayashi catalyst 173, 831, 865, 871, 875
 - -derived linear enamines 865
 - Josiphos ligand 425
- k**
- Kagan's classic ML_2 model 1145
 - Katsuki's chiral salen 364
 - Keck allylation conditions 292
 - Kerrigan's ketene heterodimerization 554
 - ketene-aldehyde cycloaddition
 - Lin's studies of 550
 - ketene-aldehyde net cycloadditions 547
 - ketene–amine adduct 539
 - ketenes 531, 533, 534, 535, 537, 538, 539, 540, 542, 543, 544, 547, 548, 550, 553, 555, 565
 - acetal 297
 - alcoholysis 530
 - -amine adduct 540
 - aminolysis 532, 535
 - catalytic enantioselective heterodimerization of 553
 - catalyzed by chiral PPY 538
 - [2 + 2] cycloaddition 541
 - -derived ammonium enolates 588
 - -derived C(1)-ammonium enolate 579
 - dimerizations 544, 551, 553
 - toward 4-alkylidene- β -lactones 550
 - Fu's alcohol additions 532
 - Fu's catalytic enantioselective coupling of 533
 - Fu's phenol addition 533
 - homodimerization 550, 553
 - Wynberg's original synthesis 539
 - α -keto esters 360, 361, 745
 - β -keto esters 618, 756
 - ketones 293, 299, 365, 387–389, 400, 405, 429, 431, 437–440, 444, 450, 538, 540, 609, 724, 730, 745, 1078
 - adducts 299
 - catalytic enantioselective alkenylation 360
 - deprotonation of 907
 - enantioselective reduction 1106
 - enolization 1251
 - reduction 452
 - silylcyanation 1221, 1224
 - with trichlorosilane 1078
 - with zinc(II) ate complexes 374
 - β -ketosilanes 906, 909
 - alkylation of enolates 909
 - enolate generated 906
 - Michael addition of 910
 - k_H/k_D values 199
 - KIEs 394, 400, 404, 405, 407, 414
 - competition experiments yield 407
 - competitive measurements 405
 - and estimated KIEs for the reduction of benzophenone 399
 - 2H measurements, at enantiotopic positions 406
 - at homotopic methyl groups 400
 - mathematical ratio 405
 - measurements 400, 408
 - – methodologies 398
 - stereochemical inversion of 406
 - kinamycins synthesis
 - C 1340
 - F 1340
 - J 1340
 - kinetic energy density 209
 - kinetic isotope effects 201, 1312

- kinetic resolution (KR) 433, 439, 459
 - of α -acyloxy-*N*-acyloxazolidinethiones 512
 - of alcohols 133, 141
 - of *sec*-allylic alcohols 464
 - of cyclic *sec*-amines 516
 - experiments of α -branched amines with anhydrides 141
 - of a racemic ketone via CBS reduction 436
 - racemic *cis*-1,2-diols 491
 - of racemic lactone 434
 - of vinyl epoxides, phosphoramidate-catalyzed 1134
- Knoevenagel condensations 1, 9, 10, 15
- Krafft modification of intramolecular Morita–Baylis–Hillman reaction 226
- Kwon's allene–alkene [4 + 2] annulation 739
 - deuterium labeling study of 735
 - theoretical analysis of 736
- I**
- lactam
 - stereoconvergent transformation of 622
- β -lactam 566, 796
 - containing compounds 563
 - heterocyclic ring 563
 - products 565
- lactam enoates
 - Ye's [4 + 2] cycloaddition 643
- lactam formation
 - via homoenolate equivalents 1332
- cis*- β -lactams 568, 569
 - Fu's catalytic enantioselective 570
- β -lactam synthesis 502, 503, 505, 506, 562, 563, 565, 573, 578, 596, 796
- lactate-derived enol ethers 321
- lactones 433, 434, 441
 - derived silyl ketene acetals 474
- β -lactones 538, 539, 540, 542, 543, 545, 552, 553, 554, 555, 557, 558, 561, 573, 795
 - applications of Wynberg's synthesis 540
 - catalytic enantioselective formation of 568
 - conversions of 543
 - Fu's net [2 + 2] cycloaddition 547
 - Song's application of 542
 - Wynberg's original synthesis 539
- δ -lactones
 - synthetic applications 639
- cis*- β -lactones 544
- lactones lactam formation
 - via enol azolium intermediates 1335
- lactonization 133, 540, 584, 588, 591
 - of acid 591
 - process 584, 585
 - protocol 591
 - ring-opening process 584
 - providing lactams, enol lactones or enol lactams 584
 - and lactamization processes 603
 - methodology, isothiurea-catalyzed 586
 - to *N*-aryl-*N*-aroyldiazenes 646
 - products 788
 - reactive intermediates/mechanistic implications 874
 - report 870
 - Seebach–Goliński topological rule 870
 - *syn*-selective additions 871
 - with α,β -unsaturated acylammonium chloride 620
 - using carbanion equivalents generate 937
- L-alanine 777
- lanthanides 544, 548
 - cocatalysts 676
 - Lewis acid 569
- Lectka's method 597
- Lewis acid (LA) 15, 16, 33, 48, 55, 56, 60, 61, 68, 72, 85, 141, 245, 339, 360, 391, 548, 561, 567, 1013, 1026, 1077, 1078
 - activation 390
 - of unsaturated carbonyls 627
 - additives 548, 582
 - base catalysis 409
 - catalysis 255, 264, 387, 391, 392, 1050, 1115
 - in silicate reactions 245
 - Lewis base activation 1155
 - mediated vinylogous addition 1070
 - NHC cocatalytic *cis*-cyclopentene formation 1335
 - quantitative expression of 62
- Lewis acid/base complexation
 - electronic redistribution 46
- Lewis acid–base interactions 61
- Lewis acid-catalyzed reactions 238, 256
- Lewis acid cocatalyst (Bi(OTf)₃) 577, 676
- Lewis acidic oxazaborolidine boron 440
- Lewis acid–Lewis base 100, 356, 364
 - bifunctional catalysis 1217, 1218
 - combinations 544
 - complexation 273
 - hypervalent bonding analysis 49
 - interactions 74
 - geometrical and electronic consequences of 44
 - Gutmann analysis 46
 - perturbation molecular orbital theory analysis 45
 - valence bond analysis 44

- natural bond orbital (NBO) analysis 51
 - phosphoramidate 362
 - rule of eight 34
 - rule of two 34
 - Lewis acid–Lewis base cooperative catalysis
 - proposed catalytic cycle 1146
 - Lewis affinity and basicity
 - scales of 58
 - Lewis base (LB) 1, 2, 12, 13, 15, 16, 21, 23, 33, 41, 59, 62, 85, 91, 93, 106, 121, 125, 127, 128, 135, 136, 139, 191, 194, 199, 211, 226, 236, 243, 270, 282, 295, 298, 299, 306, 342, 360, 534, 555, 746, 747, 968, 989, 1013, 1014, 1016, 1020, 1039, 1069, 1078, 1161
 - activated B–B bond 968
 - activated Cl_3SiH 1097
 - activation ($n \rightarrow \sigma^*$) 43, 1115
 - carbanion equivalents 905
 - activator 1190
 - in acylation reactions 459
 - adduct formation 60, 226
 - allylation of aldehydes 1016
 - from ammonium enolate 555
 - attack on mixed anhydride 135
 - benzhydrylium ions reactions 93
 - binding 341
 - with binding sites 72
 - carbonyl addition mechanism 268
 - catalysis 1, 7, 9, 11, 12, 40, 42, 44, 60, 137, 141, 251, 293, 387, 392, 858
 - activation of silicon reagents 1013
 - acyl shift of 5-acyloxyoxazoles 124
 - additions 973, 979
 - additions of amines and their derivatives 535
 - alcoholysis pathway 532
 - aldol addition, hypothetical catalytic cycle for 294
 - aldol addition of trichlorosilyl ketene 295
 - alkylations 274
 - allylation 282
 - carbanion transfer 235
 - catalyzed cyanations
 - chirality transfer 270
 - C–B and C–Si bond 967
 - C–B bond forming processes 971, 991
 - classification of interactions 43
 - coupling of ketenes 536
 - defining 40
 - to generate Brønsted base 746
 - mechanism 496
 - miscellaneous examples of 24
 - privileged chiral amines for 858
 - transformations 967
 - catalysts 124, 295, 296, 313, 321, 333, 539, 577, 586, 718, 968, 983, 1070, 1155
 - in combination with carboxylic acids 554
 - desilylation 909
 - diamine ligand 343
 - induced decomposition 135
 - interacts with π^* acceptor orbital 43
 - $n \rightarrow \pi^*$ Lewis base catalysis
 - enamine generation 858
 - silane cationic complex 270
 - with unconventional ligand structures, catalysis by 1130
 - Lewis base-activated C–Zn + C=O reactions 342
 - chiral amino alcohol-catalyzed enantioselective diethylzinc addition 343
 - Noyori's chiral amino alcohol, (–)-DAIB 344
 - RLi, RMgX , and R_2Zn , with chiral ligands
 - stoichiometric activation 342
 - Ligands
 - accelerated catalysis 42
 - cone angle 72
 - in transition metal catalysis 41
 - linear α -allylation products 1014
 - Li/Se exchange 248
 - 2-lithio-1,3-dithiane 245, 248
 - α -lithiosulfides
 - configurational stability 249
 - lithium reagents/silanes 249
 - with cyclohexenone 249
 - lithium thiolates 264
 - Liu/Romo's Michael Aldol-lactonization (NCMAL) 620
 - L- or D-tartaric acid 287
 - L-phenylalanine-derived chiral catalyst 793
 - L-proline 216, 876
 - L-threonine 215
 - LUMO
 - coefficients 223
 - lowering catalysis 806
 - lowering organocatalysts 844
 - Lu's allene–alkene [3 + 2] annulation 721
 - Lu's [3 + 2] annulation 719, 720, 722
- m**
- MacMillan
 - catalysts 813
 - first/second-generation catalysts 810
 - imidazolidinone catalysts 866
 - oxazolidinone catalyst 832
 - type iminium salts 819
 - macrolactones 442, 443

- magnesium(II) ate complexes 373
 malahensilipin A 1135
 maleimides
 – RC reaction and cyclization of 696
 mandelic acid-derived (pyridyl)
 oxazolines 1092
 Mannich reactions 183, 184, 203, 877, 1252
 – with zinc fluoride 1252
 mannose derivative
 – site-selective functionalization of 491
 Martin ligands 242, 243
 mass action law 56
 mastigophorene 433
 Matsubara, thia-Michael-lactamization
 process 636
 Mayr equation 89, 102
 Mayr–Patz equation 125
 Mayr's electrophilicity 92
 MBHADs 729, 759, 763, 765, 766, 767, 768, 791
 – alkene [3 + 2] annulation 767, 793
 – alkene annulation, proposed mechanism
 for 766
 – bearing β' -alkyl groups 791
 – in phosphine-catalyzed annulations 759
 MCA values 128
 McQuade kinetic investigations 198
 menthol
 – esterification of 460
 Me₂PINDOX 1022
 Me₃Si-CN 246, 264, 265, 269, 271
 – addition 270
 – tetrabutylammonium salt-catalyzed
 reactions 268
 – triethylamine-catalyzed reaction 265
N-mesityl-substituted amino indanol-derived
 NHC 1328
N-mesylbenzalimine 214
 metallotropic interconversion 1032
 methanolysis 565, 1238
 METHOX 286, 1024, 1136
N-(4-methoxybenzylidene)-4-methyl-
 benzenesulfonamide 223
 2-methoxyfuran
 – HX acidity, reaction efficiency 813
 π -methylhistidine-containing
 pentapeptide 488
 methyl acrylate (MA) 191, 200, 201, 211, 212,
 216, 219, 223, 227, 722
 – aza-MBH reaction of 680
 – MBH reaction of 672, 680
 α -methylallyl-SiMe₃ 256
 α -methyl and β -hydroxy groups 324
 2-methyl-2,3-butadienoate 735
 methyl 2-butyrate isomerization 720
 methyl cation affinities (MCA) 58, 68, 76, 106,
 127, 128
 – scale 69, 71
 – values 91
 methyldiphenylphosphine oxide 729
 N-methylformamide group 1093
 π -methylhistidine (Pmh)-based peptides 1259
 N-methylimidazole (NMI)
 – pipercolinic acid 1270
 N-methylimidazole-derived catalysts 489
 π -methylimidazole-functionalized lipophilic
 tetrapeptide catalyst 484
 N-methylindole 826
 – pyrrolidine-catalyzed addition 811
 4'-methylisobutyrophenone 400
 methylketene leading, to β -lactone
 – Calter's homodimerization of 551
 methyl ketone enolates
 – stereoselective addition 1044
 3-methyl-L-valine 779
 β -methyl-(Π -methylhistidine residue 483
 2-methyl-2-phenylpropanoic acid 788
 (*N*-methylpiperidin-4-yl)magnesium
 chloride 381
 α -methyl proline 183
 – α -alkylation reaction 185
 – derivative 184
 4-methylpyridine
 – with bis(catecholato)diboron 968
 N-methylpyrrole 825
 – conjugate addition reactions 821
 N-methylpyrrole alkylation, diastereomeric
 transition states 827
 O-methylquinine 553
 1-methylquinolinium
 – isoquinolinium salts 917
 4-methylthiazoliums
 – *N*-substituents 1293
 S-methylthio binaphthyl sulfonium salt 1172
 methyl vinyl ketone 203, 204, 206, 211, 746
 Mg(II)/Zn(II) ate complexes, anionic Lewis
 base activation 372
 – stoichiometric alkyl addition reaction 372
 – Zn(II) ate complexes 375
 Michael acceptors 170, 617, 628, 656, 786, 1308
 – in cyclization 698
 Michael additions 210, 221, 223, 226, 622, 645,
 716, 745, 746, 773, 868
 – activated alkenes/alkynes 746
 – anti-selective additions 873
 – cascade reactions, applications 873
 – DABCO 223

- enolate 626
- enolizable carbonyl compounds 868
- intramolecular cascade reactions 1303
- Michael annulations 752
- Michael-benzoin cascade reaction 1304
- Michael donors 618, 624, 633, 868
- Michael–Heck reaction 800
 - in total syntheses 800
- Michael–Michael-aldol-lactonization process 624
- Michael-proton transfer-enol lactonization mechanism 619
- Michael-type attack 199
- mikanecic acid 194
- Mitsunobu reaction 102, 706
- mixed double-Michael [4 + 1] reaction, mechanism of 752
- modified proline derivatives 175, 176
 - Houk–List model and proline analogs
 - – constrained bicycle proline analogs 182
 - – Mannich reaction 182, 183
 - – pyrrolidine ring conformation and 182
 - proline analogs
 - – constrained bicycle proline analogs 182
 - – Mannich reaction 182
 - – (2*S*,5*S*)-pyrrolidine-2,5-dicarboxylic acid 185
 - – triethylamine 185
- molecular orbital (MO) 33
 - diagram, of three-center–four-electron hybrids 50
 - theory 38
- mono- and bis-*N*-oxide bipyridines, synthesis of 1127
- mono- and di-*N*-oxide bipyridines 1127
- mono-carbamate-protected *cis*-1,2-diols 486
- monodentate chiral amines 270
- monodentate chiral phosphines 775, 777
- monodentate phosphines 788
- mono-, di-, and tricoordinated Zn(II) species 346
- mono-dichloroacetate derivatives of *cis*-1,2-diols 486
- monomeric cinchona alkaloids [(DHQD)₂AQN 497
- mono-*N*-oxide
 - vs. bis-*N*-oxide
 - as Lewis base catalysts, 1019
 - – enantioselectivity, effect on 1136
 - – reaction rate, effect on 1136
- mono-*N*-oxide bipyridines
 - library synthesis
 - – terpenes derived 1127
- monoprotected chiral diol intermediates 417
- α/β -monosubstituted acid chlorides 625
- monosubstituted epoxides ring opening
 - with phosphametallocene Lewis bases 1119
- monosubstituted ketenes 547, 564
 - formation 565
- monoterpene indole alkaloids 562
- Morita–Baylis–Hillman (MBH) 44, 99, 104, 191–195, 198–203, 209, 210, 212, 216, 226, 227, 502, 527, 655, 656, 676, 1269, 1270, 1316
 - acrolein 658
 - acrylates 657
 - binaphthol (BINOL)-derived chiral promoters 671
 - chiral Brønsted acids 678
 - chiral cocatalysts 676
 - chiral Lewis acids 676
 - chiral Lewis basic promoters 668
 - cinchona alkaloids as chiral amine promoters 669
 - classical and nonclassical methods for mechanistic studies associated with 226
 - cocatalyst effect in 219
 - cooperative catalysis in enantioselective 680
 - C=X electrophile 662
 - of cyclic enones and *N*-tosylarylimines 1316
 - of cyclohexenone 679
 - diastereoselective version of 210
 - dualistic nature of mechanism of 218
 - enantioselective 668
 - EWG Michael acceptor 656
 - intramolecular 226
 - ketones 656
 - kinetic studies applied to 195
 - mechanism of 195, 228
 - between methyl acrylate
 - – and aldehydes, catalyzed by DABCO 218, 220
 - – 2-thiazolecarboxaldehyde catalyzed by DABCO 221
 - Miller’s enantioselective reaction 682
 - Morita–Baylis–Hillman alcohol derivatives (MBHAD) 715
 - Pmh catalyzed 1269
 - proposed mechanisms for 211
 - α -silyl enones 661
 - thioacrylate esters 657
 - – theoretical methodologies 208
 - thiourea-derived bifunctional catalysts 672
 - under aprotic conditions 211
 - using enones as Michael acceptors 656
 - vinyl sulfones 661

- Morita-Baylis-Hillman and Rauhut-Currier reactions 1316
- Mosher's esters 401
- Mukaiyama aldol reactions 474, 1072, 1073, 1246, 1315
- Mukaiyama esterification conditions 725
- Mukaiyama–Michael reactions 1235
- addition reactions 829
 - stereoselectivity, effect of reaction parameters 830
- Mukaiyama's reagents 555, 557
- Mukaiyama-type reactions 1235
- aldol addition, of TBS enol ether 306
- Mukaiyama-type reagents 558, 592
- Mulliken charges 48
- Mulliken definition 38
- mycesterecin E 194
- n**
- natural bond order (NBO) 173, 1184
- natural products 193, 442, 538
- sulfur-containing 1171
 - synthesis 447, 737
- natural resonance theory (NRT) 51
- S_N2' displacement of the acetate group 760
- Nelson's AAC process 546
- Nelson's ketene–aldehyde coupling with the addition of lithium salt 544
- Nelson's Lewis base-catalyzed formal [4 + 2] cycloaddition 583
- neutral/anionic Lewis bases
- miscellaneous catalytic applications of 25
- neutral Lewis acids 59
- neutral zwitterionic enolates 527
- NFSI (*N*-fluorobenzene sulfonimide) 601, 1330
- NHCs (N-heterocyclic carbene) 19, 76, 104, 251, 264, 460, 507, 508, 584, 619, 832, 905, 915, 1291, 1292, 1315
- activation of silanes 1315
 - association 1001
 - binding to (pin)B–SiMe₂Ph 991
 - borosilyl adduct 1001
 - carbene catalysis 18
 - catalysis 507, 509, 978, 1292, 1304, 1319, 1320, 1328, 1333, 1340
 - acylative alcohol/diol KR/desymmetrization 508
 - additions 977
 - aza-MBH reaction 215
 - boryl addition 975
 - boryl/silyl conjugate additions 971, 999, 1002
 - C–B bond formation 979
 - conjugate additions 975
 - *trans*-esterification, mechanism 1315
 - formal [4 + 2] cycloaddition processes 584
 - hydroacylation, mechanism of 1313
 - *N*-phenyl imidazolylidene 214
 - protocol 971
 - Steglich O→C acyl rearrangements 509
 - thiazolium/triazolium based 507
 - transformation 971
 - catalyzed amidations
 - Diels-Alder reaction 1336
 - of esters with amino alcohols 1315
 - chemistry 1341
 - enolate 1337
 - generated homoenolate equivalent 1341
 - Michael acceptor 1316
 - NHC·B₂(pin)₂ complex
 - X-ray structure 999
 - NHC·B₂(pin)₂ complex formation 999
 - NHC-catalyzed aza-Morita-Baylis-Hillman
 - reversibility and selectivity of 1317
 - NHC-catalyzed boryl
 - and silyl conjugate additions 1004
 - NHC-catalyzed conjugate additions
 - cyclic and acyclic β-silylcarbonyls 994
 - NHC-catalyzed enantioselective boryl conjugate additions 981
 - NHC-catalyzed [4Y+Y₂], 1336
 - NHC–Cu-alkoxides 968
 - NHC-diboron complex 974, 999
 - NHC enolate [4Y+Y₂] manifold 1335
 - in nonclassical Lewis base-catalyzed reactions 1320
 - O- to C-carboxyl transfer reactions
 - using oxazolyl carbonates 511
 - precursors 508
 - formation of amides 515
 - redox catalysis 1330
 - singlet ground state stabilization 1292
 - in synthesis 1340
 - used in organocatalysis 1292
- nicotinamides 391
- nitroalkenes 216
- β-addition of enals 1326
 - anti-diastereoselective enamine-mediated Michael additions of 873
 - cross-RC reaction of
 - with acrylates and enones 695
 - enantioselective β-addition to 1327
- nitrogen
- containing ketones 421

- α -nitrogen-containing substituent 938
 - pronucleophiles 756
 - protection group 569
 - syntheses of 559
 - nitro-olefins 872, 874
 - addition of enamines 871
 - enamine-mediated enantioselective Michael additions 869
 - N*-2-nitrophenylselenenylsuccinimide 1162
 - 2-(β -nitrostyrenyl)allenoate 726
 - meso*-*N,N*-diacetyl-2-imidazolidinones 434
 - (*S*)-(-)-*N,N*-dimethyl-1-phenylethylamine 538
 - (*S*)-NOBIN
 - acylative KR of biaryl anilines 481
 - nonautocatalytic process 202
 - nonbonding interaction 560
 - nonchelation transition state model 327
 - noncovalent interaction (NCI) 838
 - nonenzymatic catalytic amine KR 477
 - nonenzymatic enantioselective acylation 460
 - nonlinear effects 284
 - in proline-mediated reactions 149
 - nonmetal-coordinated C(1)-ammonium enolate 568
 - nonstabilized azomethine ylide 943
 - nonsteroidal anti-inflammatory drug (NSAID) 527
 - nonthermal microwave effects 212
 - Noyori hydrogenations 387, 388
 - Noyori's catalysis 379, 380
 - Noyori's (-)-DAIB ((-)-3-*exo*-(dimethylamino)isoborneol) 340, 368, 379
 - Noyori's reaction 378
 - nucleofugalities 93, 94
 - of isothiouras 102
 - parameters 94
 - nucleophile-catalyzed aldol-lactonization (NCAL) 554, 555, 620
 - conditions 558, 561
 - derived β -lactone
 - synthetic transformations 562
 - double diastereoselective process 558
 - linearly fused and bridged tricyclic- β -lactones 625
 - mechanistic pathway for 556
 - methodology to natural product 563
 - organocascade process 624, 631
 - reaction 555, 560, 561, 562
 - Romo's NCAL methodology, applications of 561
 - nucleophile-catalyzed reactions 255
 - nucleophile(Lewis base)-catalyzed Michael proton-transfer lactonization (NCMPL) process 620
 - nucleophiles 87, 241, 247, 250, 255, 293, 297, 424, 496, 755, 760, 955, 1055
 - phosphonium ion pair, 786
 - stereochemical model 1046
 - thermodynamic affinity 87
 - π -nucleophiles 1054
 - nucleophilic addition reactions 206, 213, 264, 555, 761, 762, 1013
 - of alcohols and amines leading to carboxylic acid derivatives 527
 - nucleophilic alkoxide addition/protonation pathway 532
 - nucleophilic alkylating agents 339
 - nucleophilic ammonium enolate 558
 - nucleophilic attacks 199, 264, 566, 760, 1050
 - of allyltributylstannane 1042
 - of tertiary phosphine 194
 - nucleophilic catalysis 41, 42
 - nucleophilic counterions 557
 - nucleophilicities 85, 108, 128, 203, 339, 1045
 - of azolyldenes 1293
 - of imine 564
 - Lewis base catalyst 655
 - Mayr equation 89
 - of NHCs 1295
 - nitrogen species 535
 - *N,O*-dimethylhydroxylamine 551
 - parameters 95
 - n_{MeI} 87
 - phosphines 734
 - catalysis 800
 - PMe_3 983
 - promoter 489
 - quantitative treatments of 5, 85
 - Ritchie equation 87
 - scales 92
 - Swain–Scott and Edwards Approaches 85
 - thiophenol 534
 - tributylphosphine 734
 - nucleoside analogs 436
- O**
- octet rule 49
 - ^{18}O -labeling experiment 149, 150
 - olefins, 794
 - hydroboration 436
 - isomerization 757
 - metathesis processes 967
 - to-olefin transfer process 1176
 - oligomerization 301

- of acrylonitrile 715
 - omphadiol 562
 - Onsager solvation model 184
 - onychine/eupolauridine, natural products 687
 - organic π -acceptors 76
 - organocatalytic reactions 104, 128, 208, 219, 394, 464, 466, 471
 - chemical transformation 191
 - organocuprate reagents 534
 - organomagnesium complexes 342
 - organometallic
 - catalysis 210, 405
 - fragment 424
 - group for nucleophilic displacement 425
 - ketones 424
 - 2,3- or 3,4-syn-disubstituted pyrrolidines 586, 587
 - Ostwald's redefinition, of catalysis 5
 - 2-oxathiolanimines synthesis 1122
 - oxazaborolidine catalysis 387, 388, 389, 391, 394, 395, 407, 409, 415, 419, 429, 434, 439, 444, 450, 451, 452
 - in CBS reduction 388
 - kinetic resolution of racemic *N*-acetyl oxazolidinones 435
 - *meso*-selective deacylation of imidazolinones 428
 - reduction of ketones 445, 449, 450
 - reduction of α -phenylthio enones 420
 - oxazaborolidinium bistriflimidate 1234
 - oxazetid-2-ones
 - derivatizations of 576
 - oxazetid-3-ones 574
 - (\pm)-oxaziridine 576
 - oxaziridines 576
 - oxazolidines 750, 1108
 - thiazolidines, and pyrrolidines syntheses, through mixed double-Michael reactions 750
 - oxazolidinones 152, 167, 421, 434
 - formation 152
 - 2-oxazolidinones 505
 - oxazoline-type catalysts
 - for enantioselective reduction 1093
 - oxazolin-5-one enolate 24
 - oxazolin-4-ones 576
 - catalytic enantioselective synthesis 576
 - oxazolomycin A 545
 - oxazolone acylating agent 478
 - oxazolyl carbonates
 - Steglich rearrangement of 472
 - oxidative hydroxylation
 - via radical cation intermediates 1328
 - N*-oxides 281, 1090
 - catalysts 1025
 - crotylation catalyzed 1025
 - derived Lewis bases
 - – mechanistic studies 1136
 - Lewis bases, structure–activity relationship for 1136
 - promoters 298
 - 2-oxindolylidenemalononitriles 794
 - oxygen heterocycle-fused bicyclic β -lactones
 - via NCAL process 559
 - oxysulfenylation 1178
 - α -oxytrichlorosilyl enol ethers 305, 306
- P**
- (*R*)-pantolactone 530
 - papalucandin D, total synthesis of 1028
 - parallel KR (PKR) 463
 - Passerini reactions 1072, 1073
 - Pd-catalyzed couplings 394
 - of aryl halides 917
 - reactions 938
 - Pd-catalyzed diboron addition reactions 985
 - $\text{Pd}_2(\text{dba})_3$ -induced decarboxylation/protonation sequence
 - diastereomeric mixture 620
 - pectenotoxin-2
 - C17–C28 fragment of 837
 - 2,3-pentadienoates 726, 728, 772
 - 2,4-pentadienoic methyl ester 683
 - 2,3-pentadienone 755
 - pentafluorophenolate 601
 - N*-pentafluorophenyl-substituted NHC catalyst 1326
 - N*-pentafluorophenyl triazolium precatalyst 1340
 - penta/hexa-coordinate siliconates 242
 - 1,2,2,6,6-pentamethylpiperidine (PMP) 577, 1277
 - penta-nuclear chiral Zn(II) complex 358
 - pentaphenylcyclopentadienyl (C_5Ph_5) ring 1123
 - peptide
 - catalyzed reactions, thiazolium-based 1277
 - proline system 682
 - proposed transition models 1260
 - pericyclic process (sila-ene) 257
 - perturbation molecular orbital theory analysis 39, 45
 - phenanthryl 2-arylacrylates 1281
 - phenols 204, 533, 758, 787
 - fragment 434
 - pronucleophile 773
 - Calter's synthesis of 568

- phenyl (trans-1-phenyl-2,3-dipropylseleniranium hexafluoroantimonate) 309, 444, 1163
- phenylacetaldehyde 533, 863
- β -phenylalanine ester 1098
- phenylalanine scaffold 1092
- phenyl azomethine imine 782
- 2-phenyldithianyl transfer 238
- phenylethynylzinc species 354
- N*-phenylmorpholine–borane complex 417
- phenylphosphine 775
- N*-phenylselenenylsuccinimide (NPSS) 1161, 1162
- N*-(phenylseleno)phthalimide 884
- (phenylthio)acetic acid 572
- α -phenylthio enones 419
- phenyltrimethylsilylacetylene
 - stoichiometric reaction 262
- 2-phenyl-2-trimethylsilyl-1,3 dithiane 239, 249
- phosphabicyclo[3.3.0]octane (PBO)
 - catalyst 464
 - – KR of sec-benzylic alcohols 463
 - structure 462
- phosphaferrocene 1119
- phosphametalocene Lewis bases 1119
 - NMR data 1118
 - structure 1118
- phospha-silyl nucleophilic carbene 1291
- phosphate-catalyzed iodolactonization
 - proposed mechanism of 1201
 - representative scope of 1201
- phosphazanium fluoride 236, 255
- phosphazirconocene 1119
- phosphepine 776
- phosphinamine 787
- phosphine catalysis 194, 425, 459, 460, 461, 718, 720, 721, 726, 727, 735, 737, 739, 743, 744, 747, 754, 761
 - acylative alcohol/diol KR desymmetrization 461
 - alkyne isomerization, mechanistic proposal 769
 - allene–alkene [3 + 2] annulation 724
 - allylic substitution 764
 - annulation 741, 744, 772, 787
 - [3 + 2] annulations 719, 721, 727, 730, 760, 763, 767
 - [3 + 3] annulations 743
 - [4 + 2] annulations 734, 739
 - annulations of allenes and aldehydes 741
 - aryl/alkyl phosphine-based 460
 - catalyzed umpolung additions 754
 - cycloaddition 721
 - direct addition mechanism 749
 - generation 745
 - MBH reaction 770
 - – Michael reaction vs. base-catalyzed Michael–aldol reaction 770
 - Michael additions 745–749, 754, 786
 - – of alkynes 749
 - – pathway, proposed mechanism for 748
 - – reversibility of 748
 - Rauhut–Currier reaction of ethyl acrylate 688
 - [4 + 2] reaction, proposed mechanism 1276
 - reactions 717, 718, 737, 774
 - – of activated alkenes/allenes/alkynes 718
 - γ -umpolung addition, mechanism for 756
- phosphine-catalyzed boryl additions, to *N*-tosylimines 983–985
- phosphine-catalyzed boryl conjugate additions 981–983
- phosphine oxides 1057, 1059
 - aldol addition 1058
 - catalysts 333
 - Lewis bases, allene-containing
 - – evaluation of 1132
- phosphine oxide–siliconate complex
 - isocyanide vibration 267
- phosphines 102, 270, 460, 741, 746, 763, 766
 - nucleophilicity parameters 105
 - use of 104
- phosphino-BINOL 672
- phosphinoylimines
 - aza-MBH reaction of 668
- phosphites 102, 104
 - nucleophilicity parameters 105
- phosphitylation reaction 1263
 - tetrazole-based 1264
- phosphoramides 1016
- phosphonium
 - dienolates 719
 - dienolate zwitterions 719
 - enolates 719, 770
 - zwitterions 770
- β -phosphonium
 - detection of 747
- β -phosphonium allenolate 717, 719, 720, 745, 761, 769
- phosphonium diene species 759, 760
- phosphonium dienolates 720, 724, 730, 731, 734, 735, 739, 756, 757, 777, 781, 788
 - complex 778, 783
 - intermediate 734, 769

- phosphonium enolates 717, 746, 749
 – zwitterion 718
 phosphoramidate-derived Lewis base catalysts,
 mechanistic studies 1137
 – catalyst loading studies 1137
 – kinetic studies 1138
 – nonlinear effects 1138
 – stoichiometry studies 1137
 phosphoramides 281, 283, 284, 294, 309, 310,
 311, 327, 328, 356, 1021, 1025
 – allylation benzaldehyde 1021
 – bound silicon 324
 – catalysis 310, 317, 320, 326, 328
 – catalyzed aldol 310
 – addition 308, 326
 – reaction 311
 phosphoramidite coupling 1263
 phosphorane 267
 phosphoric acid derivative 1092
 phosphoroamide–SiCl₄ complexation 1052
 phosphorus intermediate, pentavalent 743,
 744
 phosphorus nucleophiles 558
 phosphorylation reaction, Pmh-based 1263
 phosphoryl imidazolium species 1263
 photo dimerization 287, 432
 photoredox catalysis 886, 888
 phthalan 800
N-phthalyl valine
 – Calmes's low-temperature alcoholysis 530
 – derived ketenes 530
 pileup effect 46
 Pimentel-Rundle model 49
 PINDOX catalyst 1023, 1126
 α-pinene 388, 393
 pipercolinic acid fragment 1083
 piperidine 582, 683
 (–)-pironetin 545
 4-pivaloyloxyproline 1096
 plakevulin A 561
 planar-chiral 4-(pyrrolidino)pyridine-derived
 catalyst 574
 – nucleophilic Lewis base catalyst 569, 597
N-*p*-methoxyphenyl (PMP)
 – imines 946
 – protected imines 877
 – substrates 1096
 pnictogens bases 68
³¹P NMR spectroscopic analysis 207, 208, 272,
 747, 786, 793, 1052, 1180
 – of catalytically active sulfonylating
 agent 1180
 polarity–polarizability for aprotic solvents 205
 polarizable continuum model (PCM) 74, 207,
 209, 215
 polar solvents 131, 199, 308, 397, 422, 557
 – aprotic solvents 201
 poly(acryloyl quinidine) 542
 polyaldolization 301
 polyketide synthesis 551
 polymeric cinchona alkaloids 540, 541
 polymeric MBH adducts 191
 polymerization 540
 – of MBH products 191
 polymer-supported 2-*t*-butylimino-2-
 diethylamino-1,3-dimethylperhydro-1,3,2-
 diazaphosphorine 617
 polymethacrylate backbone 1104
 polypropionates 324, 553
 polystyrene-(PS)-bound catalyst 130
 polysubstituted tetrahydrofurans
 – synthesis of 1028
 potassium trimethylsilylalkoxide–
 tetrabutylammonium chloride 237
 potential energy surface 210, 393
 P=O-triggered bifunctional activation
 – conjugate Lewis acid–Lewis base 356
 4-PPY-based catalyst 474, 477, 561
 PPY-catalyzed acetylation 130
 prenyltrimethylsilane 256
 primary amine catalyst 535
 – enantioselective intramolecular
 aldolization 877
 principal component analysis (PCA) 63
 prochiral carbonyls 438
 prochiral ketones 387, 405
 proline salt-mediated α-amination
 reaction 167
 proline 182
 – analogs 152
 – catalyst, limitations of 146, 147
 – eutectic composition of 149
 – and imidazole-cocatalyzed MBH reaction
 – Shi's proposed mechanism 681
 proline catalysis 145–146, 1269
 – aldol reaction, mechanism of 147
 – alternative to Houk–List model 158
 – effect of other additives 161
 – Seebach–Eschenmoser model 158, 159
 – water as an additive 159–161
 – α-amination and α-aminoxylation reactions,
 mechanism of
 – basic additives and proline salts 166–170
 – protic additives 161–166
 – Hajos–Parrish–Eder–Sauer–Wiechert
 (HPESW) reaction 148–150

- Houk–List model 150
 - – advances in computational chemistry 156, 157
 - – enamine intermediates 152
 - – general catalytic cycle 150–152
 - – rationalizing the origins of stereoselectivity 153–156
 - – role of enamine intermediates 152, 153
 - – stereoselectivity, rationalizing 153
 - proline derivatives 153
 - phosphoramidate 1018
 - proline enamine-based mechanism 149, 152
 - proline-mediated aldol reaction 153, 184
 - catalytic cycle 151
 - proline-mediated conjugate addition
 - reaction 170–174, 171, 172
 - peptidic proline analog 174, 175
 - stereoselectivity and diastereoselectivity of 170
 - proline/oxazolidinone/enamine pathway 169
 - proline tetrazole 177, 178, 179
 - pronucleophiles 745, 746, 749, 755, 758, 759, 760, 763, 764, 788, 789, 792
 - propanoate-derived ketene 1067
 - propargylation 281
 - propargylic alcohols 466
 - propargylic amines 480
 - propargyl silanes 260
 - N*-protected
 - indoles 505
 - oxazolidin-5-ones 925
 - silyloxyproline 1069
 - protic additives 200, 201, 202, 204, 205
 - protic solvents 201, 209, 212
 - in MBH reactions 212
 - proton acceptor 786
 - proton affinities (PA) 58, 68
 - pK_a values 128
 - protonated Brønsted base 530
 - proton-initiated carbocyclization 1187
 - proton-related scales 59
 - proton-sensitive fluorescence assay
 - for catalyst screening 483
 - proton shuttles 216, 720, 758
 - proton sponge
 - shuttle deprotonation approach 565
 - proton transfer 209, 210, 223, 689, 908
 - cascade 758
 - process 204
 - Pummerer rearrangement 419
 - pyramidalization parameter 863
 - pyranonaphthoquinones 611
 - syn/anti*-pyrrolidines 587
 - Kimpe's synthesis 611
 - 2-pyranones 741, 742, 743
 - pyridine-*N*-oxide 299
 - pyridines 95, 97, 132, 463, 475
 - accelerating effect of 459
 - benzhydrylium ion 96
 - core 441
 - desilylation of 946
 - nucleophilicity parameters 98
 - *N*-oxides 1021, 1024
 - structures acting as efficient acylation catalysts 96
 - pyridyl ketone 441
 - optimizing, CBS reduction of 442
 - pyrimidine-5-carbaldehyde 671
 - pyroglutamic acid-derived catalyst 1328
 - pyrrole 537
 - 1,2-addition of 825
 - based catalyst 466
 - derivatives 535
 - enamine π – π interaction 826
 - heterocycles 138
 - single-point minimum energy transition states 829
 - pyrrolidine ring 291, 411, 416
 - pyrrolidines 558, 586, 587, 790
 - 2-pyrrolidinone 140
 - pyrrolidinopyridine (PPY) 547
 - 4-pyrrolidinopyridine (4-PPY) core 468, 558
 - pyrrolidizines 194
 - synthesis 1337
 - 4-pyrrolines 686
 - pyrroloferrocenes 531
- q**
- quantitative analysis of ligand effects (QALE) 72
 - quantum chemical tools 74, 75
 - quantum mechanical method 208
 - quaternary C–B bonds
 - enantioselective formation of 977
 - quinidine (QD) 100, 497, 539
 - anhydride adduct 496
 - catalysts 544
 - derivative β -isocupreidine (β -ICD) 669
 - pseudoenantiomer 539
 - reaction 497
 - quinines 494, 542
 - stoichiometric quantities 495
 - quinoline nitrogen-derived ammonium salts 609
 - QUINOX 1024
 - quinoxalinones 582

- quinuclidine 202, 530
 – -catalyzed process 693
 – nitrogen 540, 542, 549
- r**
- Rab geranylgeranyltransferase 737
 racemic 1,1'-binaphthol (BINOL) with tri-*n*-butylphosphine 663
 racemic carbonyl substrates, resolution of 432
 racemic epoxides
 – kinetic resolution 1123
 racemization
 – bromosuccinate 14
 – processes 245
 – seleniranium ions
 – – effect of the aryl group on enantiospecificity 1164
 – via olefin-to-olefin transfer, studies to probe 1176
 radiation hypothesis
 – for catalysis 6
 radiation theory 7
 Rauhut–Currier reaction 683, 685, 686, 688, 703, 704, 717, 743, 1271, 1274, 1317
 – conditions 719
 – cyclization 702
 – cysteine-catalyzed 1272
 – dimerization 689
 – enantioselective 699
 – intramolecular 697
 – mixed, intermolecular 691
 – ring contraction reaction, thiol-catalyzed 1273
 – self-condensation 656
 – substrate 706
 – in total synthesis 703
 reaction progress kinetic analysis (RPKA) protocol 151, 173, 179
 Redlich–Teller product rule 394
 redox amidation reactions 1322
 – chiral NHCs, role of 1323
 redox esterification
 – NHCs (N-heterocyclic carbene) catalyzed 1325
 reduced density gradient (RDG) 838
 reductive amination 1078
 – aldehydes 1079
 reductive aza-MBH reaction 686
 reductive deoxygenation 424
 Reformatsky reaction 1315
 refractometry 57
 regiodivergent 247
 regioselectivities 130, 724, 727, 739, 776, 792
 – aldol reaction 744
 – in allylsilane–fluoride reactions 256
 – determining transition state 721
 – intramolecular aldol reaction 744
 – in intramolecular RC reactions 698
 – MBHAD–alkene [3 + 2] annulation 767
 – tandem vinylogous aza-MBH-cyclization 685
 Reissert reaction 1227
 reserpine 799
 – skeletal framework of 799
 retro-aldolization kinetics 151
 retro-Diels–Alder reaction 429
 R_FSiR₃ (Ruppert–Prakash reagents) 922
 ribonuclear protein SF3b 447
 RINMR kinetic analysis 1050
 Ritchie equation 87, 88
 Romo's Diels–Alder lactonization organocascades 630
 Romo's intramolecular nucleophile-catalyzed aldol-lactonization 555, 558
 Romo's Michael enol-lactonization 626
 rotational barriers, of methyl groups 413
 Rovis' redox amidation mechanism 1323
 Ru(bpy)₃²⁺ 888
 Ruppert–Prakash reagent 931
 ruthenium-based polypyridyl photocatalysts 888
- s**
- salen-derived chiral tetracoordinate Zn(II) complexes 354
 salinosporamide A 193, 562
 samarium diiodide 440
 SbCl₅, X-ray crystallographic analysis 47
 (S)-1,1'-Bi(2-naphthylamine) ((S)-BINAM) 681
 scandium(III) hexamethyldisilazide 568
 Schwesinger base hydrofluoride 247
 second-order Møller–Plesset
 – (MP2) perturbation theory 215
 Seebach–Eschenmoser model 164, 166, 167
 Seebach–Goliński topological rule 870, 871
syn-selective glycolate aldol reaction 1047
Z-selective Wittig olefination 1130
 selectivities
 – achieved using BINAPO 333
 – changes vs. turnover number 397
 selenenyl reagent (RSeX) 1161
 seleniranium ions
 – protonation, ester enolate 530
 – intermediate 1162
 – racemization 1164
 – transfer between olefins 1164

- α -selenoaldehydes 885
- selenocarbonates to selenoethers conversion
 - stereospecificity 1166
- selenocyclization products 1163
- selenocyclofunctionalizations 1159
- selenoetherification
 - chiral Lewis bases survey for 1167
- selenofunctionalization
 - by using enantiopure selenenylating agent 1157
 - using enantiopure selenenylating agents 1160
- selenofunctionalizations 1156–1170, 1159, 1173
 - Lewis base-catalyzed 1159
 - using enantiopure selenenylating agents 1158
- selenolactonization
 - Lewis base-catalyzed 1162
- separated ion pairs (SIPs) 245
- serotonin antagonists 293
- SF₅-substituted alkynes 950
- Shi's BINAM-derived thiourea catalyst 681
- Shi's synthesis of functionalized acrylates 759
- Si-C-acyl species, enolate generation 906
- SiCl₄ 1058
 - allylation of aldehydes 1043
 - catalyzed by phosphoramidate 1068
 - complexation enthalpies 49
 - direct aldol addition 1059
- SiCl₃ fragment 1073
- SiCl₃OTf 1062
 - direct Aldol addition 1061
- SiCl₄/phosphoramidate mixtures 1051
- Si-C-X activation
 - potentially catalytic cases 936
- [2,3]-sigmatropic rearrangement
 - to furnish homoallylamine 943
 - sulfonium salt 952
 - trimethylsilylmethyl sulfonium salts 952
 - α -trimethylsilylsulfonium salt 953
 - α -trimethylsilylsulfonium salt trans-270
- silanes
 - activation of 937, 1077
 - treatment 234
- silaphilic Lewis bases 233
- silaphilic nucleophile 238
- siliconates
 - ammonium ion pair 614
 - carbanions, reactivity 245
 - intermediate, pentacoordinate 1136
 - as Lewis acids 244
 - Me₄SiF⁻ 247
 - pentacoordinated 244, 284
 - reactivity 266
 - transition structure 285
- siliconates/carbanions, reactivity 245
- siliconates Me₃Si(CH=CH₂)F⁻ 247
- silicon-based Lewis acids 1039
- silicon-based Lewis base-catalyzed anion transfers 238
- silicon complexes
 - hybridization scheme/orbital picture of 50
- silicon derivatives
 - Lewis base activation of 1040
- silicon-induced cascade reaction 955
- siliconium ion
 - intermediate 1050
 - pentacoordinated 1041
- silicon-Pummerer rearrangement product 918
- siloxo-substituted carbenium ion 235
- silyl anion species, generation of 992
- silyl-based carbon nucleophiles 238
- silyl cross-benzoin reaction
 - cyanide-catalyzed 1300
- silylcyanation of epoxides 274
- silyl dienol ethers
 - vinylogous aldol addition 1068
- 2-silyl-1,3-dithianes 254, 945, 955, 956
- silyl ketene acetals 474, 475, 1049, 1050, 1057
 - to benzaldehyde catalyzed 1046
 - C-acylation of 474
 - isothiourea-catalyzed C-acylation 505
 - *O*- versus C-acylated products 474
- N,O*-silyl ketene acetals 1069
 - stereoselective addition 1069
- N*-silyl ketene imines
 - to aromatic enones 1055
 - nitrile derivatives 1054
- silyl ketenes
 - Whitehead's enantioselective coupling 534
- N*-silyl vinylketene imine 1056
- SIP carbanions 250
- SIP lithium reagent 249
- SIPr /aldehydes reaction
 - isolated intermediates 1297
- SiX₃-based reagents 1013
- S-methyl group transfer 1172
- Smith's *anti* beta-lactam synthesis 571
- Smith's Michael-proton transfer–enol lactonization 616, 618
- Sn-C-X
 - alkylation, arylation, and vinylation 958
 - carbanion generation 956
- Sn(IV)–phosphoramidate complexes 311
- S_N2' displacement 445, 763, 764, 773

- S_N2 displacement of the bromide 766
 S_N2 mechanism 72
 S_N2 pathway 1113
 $S_N2' - S_N2'$
 – cascade 765
 – displacement cascade 763
 – – mechanism 764
 – formation of the ylide 766
 sofosbuvir 436
 solute scale 62
 solute–solvent interactions 207
 solvent
 – basicity scales 62, 63
 – -dependence of acylation reactions 131
 – dependence of reactivity
 – dependence of selectivity
 – – in catalytic reductions 397
 – – of para-substituted acetophenone 397
 – effects 62, 209
 – – corrections 209
 – – temperature 395
 – – upon selectivity 396
 – -induced dissociation 245
 – rule 530
 – scale 62
 – -separated ion pair 249
 α -SO₂R silanes 918
 – carbanion derived 919
 spectroscopic basicity scales 76
 spillover effect 47
 spinosyn A synthesis
 – via a macrocyclization, Diels–Alder, RC
 reaction sequence 704
 Spivey's transition state model 470
 spongistatin
 – C6–C13 fragment of 986
 stabilized benzhydrylium ions 863
 stable allyl siliconates 259
 stable hexacoordinate dianionic triorgano
 siliconates R₃SiX₃²⁻ 243
 stable penta-organosiliconate 241
 π -stacking 483, 1266
 stannylated sulfide
 – [2,3]-thia-Wittig rearrangement 960
 Staudinger reaction 564
 Steglich esterification 136
 Steglich rearrangements 24, 504, 505,
 511, 512
 – with zwitterionic Lewis basic catalyst 513
 stephacidin B 447, 448
 stereocontrol
 – aldol reactions 534
 – allylation 281
 – in the proline-mediated conjugate addition
 reaction 172
 stereoconvergent
 – crotylation 1238
 – reactions 1241
 stereodivergence 588
 – approach 630
 stereoselection 389, 393, 398
 – acyl transfer protocols 464
 – allylation 283
 – bisvinylogous 1071
 – – aldol addition 1071
 – – for catalytic 1049
 – – for direct aldol addition 1060
 stereospecific Claisen rearrangement 449
 stereospecificity
 – in desilylation 248
 steric-blocking model 173
 steric repulsion 388, 396, 403
 – at transition state, giving rise to inverse KIE
 using DIP-Cl reduction 403
 Stetter reactions 508, 1307, 1311, 1312, 1328,
 1340, 1341
 – of acrylates 1312
 – diastereoselective 1310
 – first enantioselective 1311
 – intramolecular version 1309
 – triazolium-catalyzed 1278
 – using achiral Lewis base catalysts 1310
 Stetter/Umpolung reactions 1276
 stilbene diamine
 – -derived phosphoramidate (S,S) 307
 stilbene-1,2-diamine-derived catalyst 314, 327
 stilbene-1,2-diamine-derived
 phosphoramidate 318
 Strecker reaction 1224, 1225
 – of ketimines 1228
 Strecker-type reaction 355
 – RC dimerization of 691
 substrate–catalyst interactions 779, 780, 785,
 786
 substrate racemization rate 433
 sulfenoaminations 1189, 1190
 – endo–exo isomerization studies 1191
 sulfenoaminocyclizations 1190
 sulfenoetherification 1189
 – of 4-octene 1183
 – mechanistic studies 1179
 sulfenofunctionalization 1170, 1172, 1180,
 1181
 sulfenylating agent
 – independent generation 1182
 sulfenylations

- amide moiety 1172
 - prochiral alkenes 1172
 - reactions 1172
 - using chiral auxiliaries 1172
 - sulfinate esters synthesis
 - cinchona alkaloid catalyzed 1268
 - sulfonamide-derived catalysts 1026
 - sulfonamides 579
 - as Lewis base catalysts 1019
 - sulfone moiety
 - *p*-nitrophenyl group 698
 - sulfonium salt
 - [2,3]-sigmatropic rearrangement 951
 - sulfonium ylides
 - [2,3]-sigmatropic rearrangement 951
 - sulfonylation 489
 - sulfonyl chlorides 576, 577
 - N*-sulfonyl imines 563, 593
 - sulfoxides/amides, as catalyst 281
 - carbonyl compounds 919
 - for enantioselective allylation 1025
 - Lewis base catalysts 1019
 - *N*-oxide groups
 - – reductive amination with a concomitant reduction 1081
 - sulfur pronucleophiles 758
 - sulfur–selenium orbital overlap 1159
 - Suzuki coupling 445
 - Suzuki–Miyaura-type cross-coupling reactions 363, 983
 - Swain–Scott correlation 86
 - Swain solvation constants 196
 - Swern oxidation 434
 - synergistic catalysis
 - chiral oxazaborolidinium salts 1234
 - chiral ruthenium catalyst 1233
 - enantioselective silylcyanation 1233
 - synthesis
 - (+)-dactylolide 1342
 - (±) hirsutic acid C 1341
 - maremycin B 1341
 - (–)-paroxetine 1342
- f**
- TADDOLate–Mg(II) salts 343
 - TADDOLate–Ti(IV)-catalyzed dialkylzinc addition 368
 - tandem cyclization 773
 - TangPhos-catalyzed γ -umpolung addition, Zhang's proposed mechanism for 788
 - Tebbe/Diels–Alder reactions 737
 - TEMPO radical 1324
 - tensimetry 57
 - terminal epoxides
 - kinetic resolution
 - – by enantioselective fluoride addition 1145
 - with triphenylphosphine-catalyzed TMSCl 1117
 - tertiary amine-catalyzed enantioselective Michael addition–lactonization/lactamization processes 584
 - tertiary amine-catalyzed formal [2 + 2] / [3 + 2] cycloadditions 579
 - tertiary amine 1,4-diazabicyclo[2.2.2]octane (DABCO) 655
 - tertiary amine Lewis bases 538
 - tertiary amine *N*-oxide 1232
 - tertiary amines
 - *N* parameter 101
 - tertiary α -chloroesters 597
 - tertiary phosphines
 - catalysts 746
 - tertiary propargyl alcohols 363
 - tethered acidic malononitrile 739
 - tethered electrophile–nucleophile system 770
 - β -tetraalkylammonium enolate 226
 - tetraalkylammonium halides 957
 - tetrabutylammonium acetate 263
 - tetrabutylammonium alkoxides 237, 255
 - tetrabutylammonium bis(biphenyl) methylsiliconate 241
 - tetrabutylammonium cyanide (TBACN) 910
 - compared with Me₃Si–CN–TBAF/KCN–12-crown-6, 246
 - tetrabutylammonium difluorotriphenylsilicate (TBAT) 1240
 - tetrabutylammonium fluoride (TBAF) 236, 906
 - -catalyzed reaction 250
 - stoichiometric amounts 250
 - tetrabutylammonium phenoxide 237, 248
 - tetrabutylammonium salts 247, 269
 - tetrabutylammonium triphenyldifluorosilicate (TBAT) 236, 907, 928
 - tetracoordinate borohydride compounds 402
 - tetrahydrofuran (THF)
 - IEFPCM solvent model 413
 - solvent 403
 - mechanism of formation of 733
 - tetrahydropyrazolopyrazolones 731, 732, 782
 - tetrahydropyridines 734, 737, 783, 798, 799
 - tetramethylammonium fluoride (TMAF) 931
 - tetramisole 586
 - tetramisole hydrochloride (TM) 584
 - tetrapeptide catalyst 483, 485

- tetravalent phosphonium enolate zwitterions 717
- tetravalent phosphonium zwitterions, preparation of stable 718
- tetravalent phosphorus center 718
- thermodynamic 91
- aspects of Lewis basicity 76
 - of binding simple electrophiles 124
 - characteristics 42
 - data 76
 - decomposition
 - of ^2H KIEs 415
 - halogen bond scales 60
 - Lewis basicity scales 64, 73
 - parameters 58
 - properties, of MBH reaction 212
 - scales 59, 62, 76
- thermodynamic scales
- of Lewis affinity and basicity 56
- thia-Michael lactamization process of Matsubara 637
- [2,3]-thia-Wittig rearrangement 960
- 2-thiazolecarboxaldehyde 219
- thiazolidines 750
- 4-thiazolidinone 140
- thiazolium-based carbenes 508
- thiazolium-catalyzed benzoin 1298
- condensation 19
- thiazolium deprotonation 19
- thiazoliums
- acidities of 1294
- thiazolium salt-catalyzed benzoin condensation 19
- thiazolium salt-catalyzed C–C bond formation and cleavage 19
- thiazolylidene-catalyzed benzoin reaction 1298
- thienoates
- in intramolecular RC reaction 705
- thiiranium formation 1172
- thiiranium ions, 1176
- exchange reactions 1176
 - intermediates 1170
 - by Lewis bases 1175
 - possible racemization pathways 1174
 - racemization 1176
 - unimolecular racemization of 1174
- thiiranium ions, possible racemization pathways 1174
- N*-thioacyl imines 583
- thioamide catalysts 487
- thioamide-containing tetrapeptide 483
- thiocarbonyl ylide 946
- thiocyanate-catalyzed reactions 268
- thioesters 534
- proposed rationalization 1063
- thioformamides 488
- thioimide methylides
- cycloaddition of 940
- thionoformylation 486
- thiophenol 534
- enantioselective addition 534
- thiourea
- -based chiral phosphine 779, 780
 - catalysts 495
 - group 792, 793
 - -tertiary amine catalyzed reaction 216
- threonine-derived phosphine 791
- tin-Li exchange 958, 960
- Tischenko-type processes 301
- titanium(IV) fluoride catalysis
- transition structure 1238
- TMSCF₃
- with heteroatom electrophiles 934
 - to hexafluoro ketamine and azirine 930
 - to *N*-aryl imines 929
 - to nitrones 930
 - to *N*-phenyl imines catalyzed by TBAT 930
 - with SO₂ and CO₂ 935
 - α,β -unsaturated carbonyl compounds, 1,4-addition of 931
- TMSCF(SO₂Ph)₂ with aldehydes 919
- O*- to *C*-acyl/carboxyl transfer 471
- O*- to *C*-carboxyl transfer reaction
- achiral NHC precursor 510
- α -tocopherol 894
- enantioselective total synthesis of 895
- Tolman cone angle 72
- N*-toluenesulfonyl aziridines 955
- N*-toluenesulfonyl benzaldimines 727
- electrophile 671
- tosyl *tert*-butylimine 737
- N*-tosyl thioureas 700
- total syntheses
- (+)-geniposide 797
 - (–)-hinesol 796
 - (\pm)-hirsutene 797
 - (\pm)-hirsutine 799
 - (+)-trachelanthamidine 798
- transesterification reactions
- NHCs (*N*-heterocyclic carbene) catalyzed 1314
- transition state 196
- arrangement 548, 560
 - lateness 400
 - models 202, 324, 329, 778, 779, 783, 1286

- in Zn(II) ate-alkyl addition 375
- transition structures 281, 283, 291, 320, 323, 328, 396
- for the allylation reaction 289
- for $\text{BH}_3\cdot\text{DMS}$ reduction 412
- trialkoxysilanes 1105
- enantioselective reduction of ketimines 1105
- trialkylmagnesium(II) ate complexes ($[\text{R}_3\text{Mg}]^-[\text{Li}]^+[\text{LiX}]$) 373
- trialkylphosphines 461
- trialkylphosphonium-containing zwitterion 194
- trialkylsilyl enolates 1049
- trialkylsilyl fluorides 241
- triaminopyridine 128
- triarylphosphines 104
- 1,2,4-triazole 514
- formation of amides 515
- triazoliums
- acidities of 1294
- motif 1291
- triazolium scaffold 1291
- triazolylidene NHC 1295
- tributylphosphine 721, 724, 731, 744, 749, 761, 772
- α,α,α -trichloromethyl methyl ketone 540
- N*-2,4,6-trichlorophenyl-substituted NHC 1328
- trichlorosilane 293, 1078, 1096
- aldehydes
- reductive amination of 1078
- enantioselective reduction of functionalized ketimines
- imines 1103
- enantioselective reduction of ketimines 1083
- chiral amides as catalysts 1088
- chiral formamides 1083
- computational studies 1093
- (pyridyl)oxazolines as catalysts 1092
- sulfenamides and phosphoramides as catalysts 1091
- enantioselective reduction of ketones 1105
- Lewis base-catalyzed enantioselective reduction 1096
- of α -imino esters 1096
- of vicinal chloroimines 1095
- synthetic applications of enantioselective reduction of imines 1106
- trichlorosilyl cationic species 1042
- trichlorosilyl chlorohydrin 1043
- trichlorosilyl enol ethers 293, 295, 301, 304, 306, 307, 309, 311, 314, 317, 321, 324–326, 328, 333, 1057
- trichlorosilyl ether 305
- of homoallylic alcohol 1042
- trichlorosilyl ketene acetal 294, 297
- trichlorosilyl moiety 293
- trichlorosilyl reagents 331
- trichlorosilyl triflate 333, 1060
- 1-trichlorosilyl-4-trimethylsilyl-2-butene 1027
- tricyclohexylphosphine 191, 743
- triethoxysilyl acetylene 1032
- triethylfluorosilane 237
- triethylsilane 447
- triflic acid-assisted dehydration of selenides 1165
- α -trifluoromethylation 889
- trifluoromethylations 253
- of amino-ketones 252
- mechanisms 252
- reactions 253
- trifluoromethyl-bearing stereogenic center 590
- trifluoromethyl ketones 730, 741
- enantioselective alkynylation of 366
- 4-trifluoromethylphenylacetic acid 590
- 2-trifluoromethylphenyl seleniranium ion intermediate 1166
- N*-triflyl imines 569, 578
- trihalosilanes
- Lewis base-catalyzed allylation 1014
- triisopropylsilyl ketene imines 1054
- to aliphatic aldehydes 1054
- trimethylaluminum, with benzophenone 349
- trimethylamine-catalyzed reaction 212
- trimethyl(fluoroalkyl)silanes 932
- with alkyl halides 933
- with aryl, benzyl, and allyl halides 933
- with heteroatom-based reagents 935
- trimethyl(perfluoroalkyl)silanes
- to carbonyl compounds 923
- to imines 929
- trimethylphosphine 213, 741, 746, 748, 752, 755, 798
- trimethylsiloxybenzhydryl group 862
- 2-(trimethylsiloxy)furan 765, 791
- 2-trimethylsilyl-1,3-dithiane (TMS-dithiane) 944
- O*-trimethylsilyl (TMS) 544
- diaryl prolinol, 878, 884
- TMS enol ethers
- aldol addition 1044

- O-TMS quindine 586, 588
 - α -TMS-thioethers, to carbonyl compounds 947
 - α -trimethylsilyl acetate 914
 - arylation, via nucleophilic addition and oxidation sequence 914
 - trimethylsilylacetonitrile
 - to aldehyde 916
 - to C=N bond 917
 - α -trimethylsilyl- α,β -unsaturated ketones as 1-acylethenyl anion synthons 909
 - trimethylsilylbenzyl phenyl thioether to cyclohexenone 948
 - trimethylsilyl chloride 424, 688
 - trimethylsilyl cyanide (TMSCN) 1216
 - α -trimethylsilyl cyclopropane nitrile 915
 - α -trimethylsilyl cyclopropyl ketone 908
 - 2-trimethylsilyl-1,3-dithiane 946
 - to imines 947
 - to α,β -unsaturated ketone and ester 949
 - 2-trimethylsilyl-1,3-dithiolanes and 2-trimethylsilyl-N-boc-thiazolidines 248
 - trimethylsilyl enol ethers 311, 1045
 - of acetaldehyde 1044
 - α -trimethylsilyl epoxy lactone 911
 - α -trimethylsilyl epoxy sulfones, transannular cyclization 920
 - α -trimethylsilyl ketone 906, 910
 - fluoride ion-induced desilylation 909
 - N-[(trimethylsilyl)methyl]amino ethers
 - synthetic application 942
 - β -(trimethylsilylmethyl)amino- β -(methylthio) acrylonitrile 943
 - N-[(trimethylsilyl)methyl]azinones to ketones 939
 - α -trimethylsilylnitriles 918
 - to carbonyl compounds 915
 - desilylation 915
 - trimethylsilyl(phenylthio)(phenyl) methane 239
 - α -trimethylsilyl phosphonate, transannular cyclization 920
 - O-trimethylsilylquinine 583
 - α -trimethylsilyl sulfinylcyclopropane
 - desilylation of 918
 - α -trimethylsilylsulfonium salts 953
 - desilylation of 951
 - [2,3]-sigmatropic rearrangement 954
 - trimethylsulfoxonium iodide 14, 440
 - trimethyl(trifluoromethyl)silane 251
 - tri-*n*-butylphosphine 104, 691, 696
 - tri-*n*-butylphosphine-catalyzed RC reaction of acrylonitrile and ethyl acrylate 693
 - triorgano siliconates
 - Lewis acidity 266
 - triphenylphosphine
 - -catalyzed C–C bond formation 715
 - triphenylphosphine oxide (TPPO) 285, 1122, 1218, 1234
 - triple ion reaction 245
 - tris(2,6-dimethoxyphenyl)phosphine (TDMPP) 661
 - tris(dimethylamino)sulfonium carbanion
 - quantitative formation of 249
 - tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) 236, 915
 - tris(2,4,6-trimethoxyphenyl) phosphine (TTMPP) 915
 - tris(trimethylsilyl)methyl lithium (Me_3Si)₃C-Li 245
 - N- τ -tritylhistidine 1266
- u**
- γ -umpolung 760
 - α -umpolung addition 761
 - of alkyl propiolates 761
 - mechanism for 761
 - β -umpolung addition 758, 760
 - γ -umpolung addition 755, 772
 - β -umpolung addition, mechanism for 758
 - α -umpolung adduct 762
 - β -umpolung methodology 759
 - γ -umpolung–Michael
 - addition 752
 - annulation 757
 - γ -umpolung products 757
 - β -umpolung reaction 758
 - umpolung reactions 1276
 - γ -umpolung reactions 757, 758
 - unactivated double bonds
 - hydroacylations 1312
 - unsaturated acid chlorides
 - Ye's formal [4+2] cycloaddition 642
 - α,β -unsaturated acylammonium
 - salts 614, 628, 629
 - α,β -unsaturated acylammonium chlorides 620, 622
 - α,β -unsaturated acylammonium fluorides
 - [3+2] annulation of 614
 - α,β -unsaturated acylammonium salt 617, 633
 - α,β -unsaturated acyl azolium 1338
 - reactions of 1338
 - α,β -unsaturated acyl fluorides
 - Fu's net [3+2] annulation 613
 - α,β -unsaturated aldehydes 1080

- dienamine-mediated enantioselective catalytic γ -amination of 893
 - and ketones 922
 - unsaturated amides
 - chlorocyclization
 - – with (DHQD)₂PHAL 1197
 - α,β -unsaturated carbonyls 527
 - α,β -unsaturated esters 591, 617, 655, 913
 - α,β -unsaturated iminium ions
 - form cycloaddition products 805
 - α,β -unsaturated ketimines 593
 - α,β -unsaturated ketophosphonates 592
 - α,β -unsaturated δ -lactones 210
 - α,β -unsaturated Weinreb amides 975
 - β -unsubstituted Michael acceptors 1312
- v**
- valence bond analysis 44
 - valences
 - Lewis definitions of 34
 - valine-derived catalysts 1094
 - valinol-derived catalyst 421
 - van der Waals radii 411, 412, 883
 - van't Hoff equation 58
 - van't Hoff plots 59, 748
 - Vedejs' phosphine catalysts 462
 - Vellalath/Romo's Michael-proton-transfer lactonization/lactamization 620
 - vibrational coupling constants 394
 - vinyl epoxide
 - phosphoramidate-catalyzed kinetic resolution 1134
 - 2-vinylidenesuccinate 783, 784, 798
 - vinyllogous aldol additions 1066, 1070
 - vinyllogous aza-MBH adducts
 - tandem photoisomerization–cyclization of 684
 - vinyllogous aza-MBH–isomerization–cyclization sequence 685, 687
 - vinyllogous aza-MBH–photoisomerization–cyclization sequence 687
 - vinyllogous Morita–Baylis–Hillman reaction
 - tandem vinyllogous aza-Morita–Baylis–Hillman Reactions
 - – with bis-activated dienes 685
 - in total synthesis 687
 - vinyllogy, in enamine-mediated catalysis 892, 893
 - vinylphosphorus 794
 - ylide, formation of 763
 - vinyl sulfones
 - intramolecular RC reaction 699
- w**
- Wacker oxidation 7
 - waihoensene
 - intramolecular RC reaction 697
 - Warshel's model 392
 - water, for amine catalysts
 - pK_{aH} values 812
 - Weinreb amide 551, 978
 - Gaunt's synthesis 608
 - Werner classification, of molecular complexes 35
 - wind shield-wiper effect 819
 - Winterfeldt reaction 744, 745, 761
 - proposed mechanism of 745
 - Winterfeldt's synthesis, of γ -lactones 732
 - Wittig–Horner–Wadsworth–Emmons olefination 698
 - Wittig olefination 586
 - Wittig-type olefin synthesis 975
 - Wolff–Kishner reduction 434
 - Woodward–Hoffman rules
 - [6 + 2] cycloaddition 891
 - Wynberg β -lactone synthesis 539
 - Wynberg process 542, 548
 - ammonium enolate model 534
 - Wynberg's model 535
 - Wynberg's net [2 + 2] cycloaddition 542
- x**
- xanthanolides 547
 - xanthenone 770
- y**
- Yamaguchi esterification 133, 134
 - Yamashita's chiral-4-DMAP catalyst 470 [3Y+Y2]
 - annulation of enals and aldehydes 1332
 - annulations of enals and imines 1333 [3Y+Y3]
 - cycloaddition with the homoenolate 1334 [4Y+Y2]
 - reaction 1339 [4Y+Y2] cycloaddition 1335
- z**
- zero-point energy 402, 404
 - Ziegler-Natta alkene polymerization chemistry 7
 - Zimmerman–Traxler model 317
 - zinc chloride-catalyzed Grignard addition reactions 376
 - zinc(II) ate-catalyzed alkyl addition 376
 - zirconium alkoxide complex 1113

- ZnCl₂-Me₃SiCH₂MgCl-RMgX·LiCl system 379, 381
- ZnCl₂-RMgCl system 381
- ZnCl₂-RMgX system 379
- Zn(II) ate-catalyzed diastereoselective cyclopentyl addition 377
- Zn(II) ate-catalyzed piperidinyll addition 382
- zwitterionic, 743
 - adducts 213, 215
 - ammonium enolates 588
 - catalysts solubility 876
 - enolate 203
 - - adduct 207
 - intermediates 203, 207, 212, 213
 - - stabilization of 197
 - nucleophilic carbon 200
 - phosphonium 692
 - - enolate precursor 697
 - species 715
 - structure 731
- zwitterionic catalysts, solubility of 876
- 1,5-zwitterionic sulfonium-enolate 1275

