

Index

a

- 1-acenaphthenone 457
- acetoxy- and amino-
trifluoromethylthiolation of
alkenes 426
- achiral fluoro-organophosphines 766
- adamantyl thioperoxide reagent 376
- AgSCF₃/K₂S₂O₈-mediated
decarboxylative
trifluoromethylthiolation 392
- air-stable and recyclable Pd(I)
catalyst 354
- air-stable copper trifluoromethylthio
complex (bpy)CuSCF₃ 314
- aliphatic ketones 462
- aliphatic pentafluorosulfanyl (SF₅)
alkenes using SF₅X
photochemical
activation 574–575
- S₂F₁₀ 572
- SF₅Br 572
- SF₅Cl 572
- thermal reactions of 574
- triethylborane 577
- alkenes using SF₆ 572
- alkenyl compounds 602
- β-haloalkyl-perfluorosulfanyl
compounds
- aldehydes 581–582
- C₂-building blocks 588–601
- γ-SF₅-α,β-unsaturated
aldehydes 586–588
- halogen substitution
reactions 580–581
- vinyl-SF₅ compounds 583–586
- oxidation of 606
- aliphatic trifluoromethylthioether 374
- alkenyl-SF₅ compounds
acetylene and
dehydrochlorination 602–604
- alkyl halides 92, 95–96, 122, 258, 275,
311–312, 434–436, 438, 469, 518
- alkylidene(difluoro)cyclopropanes 159
- alkyl–Pd(IV)–OCF₃ complex 252–253
- alkyl triflates 258
- alkyl triflones 514–520
- applications 517–520
- preparation 514–517
- alkyl trifluoromethyl (or perfluoroalkyl)
sulfoximines 681
- alkyl trifluoromethyl sulfoxides [(Alk)
S(O)CF₃]
applications 491–492
- preparation 489–491
- alkyne-based aryl iminosulfur
oxydifluoride 670
- alkynes, difluoromethylation 79–82
- alkynyl and vinyl triflones
applications 510–513
- preparation 510
- alkynyl trifluoromethyl
selenoethers 705, 711
- 2-alkynylnitroarenes 81
- 2,3-allenoic acids 396–397, 407
- allylic trifluoromethyl sulfides 407
- α-aryl-β-(trifluoromethylthio)
acrylates 381
- α-trimethylsilyldifluoroacetamides 31

- α,α -diaryl allylic alcohols 407
- α,α -difluoro- β -aminophosphonic acids 787
- α,α -difluoro β -carbonyl and β -enol ether sulfoxides 501
- α,α -difluoro β -carbonyl or β -alkyl sulfoxides 503
- α,α -difluorobenzyl phosphonates 776
- α,α -difluoro- γ -aminophosphonates 59
- α,β -unsaturated carboxylic acids 408–410, 535
- α -bromoketones 282, 439, 442, 467, 469, 471, 779, 782–784
- α -CF₂-alcohols 524
- α -chloro- β -fluoroalkylselenolation of alkenes 710–711
- α -chloro- β -trifluoroalkylselenoethers 709
- α -diazoketones 425, 427, 702
- α -fluorinated cyclopropylphosphonamides 772
- α -fluorinated γ -aminophosphonates 772
- α -fluoro- β -aminophosphonates 791
- α -fluoro- β -ketophosphonates 771
- α -fluorovinylphosphonates 772
- α -haloketones/ α -diazo esters 698
- α -pentafluorosulfanyl aldehydes 581–582
- α -phenyl- and α -methylstyrenes 573
- α -(4-pyridyl *N*-oxide)-*N*-*tert*-butylnitrone (POBN) 246
- α -SCF₂PO(OEt)₂ ketones 467
- α -SCF₃- β -substituted carbonyl compounds 421
- α -SCF₃-substituted esters 375, 437
- α -SCF₃-substituted ketones 393, 439
- α -trifluoromethylthio acetophenones 408, 410
- α -trifluoromethylthiolated esters 436
- α -trifluoromethylthiolated ketones 417, 436
- α -(trifluoromethylthio)phosphonium ylides 376
- AMBN (2,2'-azobis(2-methylbutyronitrile)) 464
- Amii's method 26
- anhydrous proton-exchange membranes 784
- anionic SCF₃ reagents 405–411
- anthracene 344
- anti*-Markovnikov process 393
- arenesulfinyl chlorides 678
- aromatic and aliphatic trifluoromethylthiolated alkynes 387
- aromatic compounds
 - aryl boronic acids 352–354
 - aryl diazonium salts 347–349
 - aryl halides 354–357
 - aryl metallic species 350–351
 - aryl triflates 349–350
 - di(hetero)aryl- λ^3 -iodanes 357–358
 - direct C–H functionalization 343–347
- aromatic disulfides 551–552, 554, 556, 558, 611–612
- aromatic thiols 451, 554–556
- Ar-SF₄-Ar derivatives 614–615
- Ar-SF₄-R derivatives 615–617
- aryl and heteroaryl difluoromethyl sulfones [RSO₂CF₂H]
 - applications 522–529
 - preparation 520–522
- aryl and heteroaryl halodifluoromethyl sulfones 529–530
- aryl 3-aryl-2-propynyl ethers 394, 395
- aryl boronic acids 26, 131, 281, 323–324, 343, 352–354, 368, 464, 480, 526, 650–651, 653, 662–663, 704, 776, 778
- aryl diazonium salts 26, 237–238, 347–349, 453, 468–469, 471, 653, 778–779
- 4-aryl (*E*)-but-3-enoic acids 428
- aryl halides 6–7, 10, 16, 26, 31, 131, 311–312, 316, 343, 347, 350, 354–357, 368, 434, 480, 699, 703, 705–706, 752–753

- arylmercaptodifluoromethylacetic acids 292–293
 - arylmercaptodifluoromethylene radical 293
 - aryl metallic species 343, 350–351, 368
 - arylpropynones 393–395
 - aryl-SCF₂PO(OEt)₂ derivatives 468
 - aryl S–CF₃ sulfilimines 676
 - aryl S–R_F sulfilimines 677, 683
 - aryl sulfonyl fluorides 623, 624, 626, 628–630, 638–641, 643, 649–651
 - arylsulfurchlorotetrafluorides
 - aryl bis- and tris(sulfur chlorotetrafluorides) 560
 - arylsulfur pentafluorides
 - anhydrous HF 561
 - antimony fluorides 561
 - Cl/F exchange reaction of 564
 - Umemoto's method and KHF₂ 562
 - zinc(II) fluoride 561
 - TCICA 565, 567
 - trans*-configuration 558
 - arylsulfur pentafluoride synthesis 553
 - aryl trichloromethyl thioethers 292
 - aryl triflates 316, 343, 349–351, 368, 507, 510
 - aryl triflones [ArSO₂CF₃]
 - applications 508–509
 - preparation 505–508
 - aryltrifluoromethylodanes (ArICF₃X) 294
 - aryl trifluoromethyl sulfides 304, 344, 347, 479
 - aryl trifluoromethyl sulfoxides [ArS(O)CF₃]
 - application 478–484
 - preparation 478
 - aryl trifluoromethyl thioethers 295–296, 348, 482
 - aryl (trimethylsilyl)difluoromethyl sulfones [ArSO₂CF₂TMS] 536
 - atom transfer radical addition (ATRA) 56, 108, 128, 374
 - aza-heteroaromatic thiols 728
 - azidotrifluoromethane (CF₃N₃) 750
- b**
- base-mediated nucleophilic difluoromethylation 525
 - benzimidazole 180, 242–243, 726, 732, 737
 - benzothiophenes 364–365, 469, 631, 709
 - 1,4-benzoquinone (BQ) 261, 513
 - benzyltrifluoromethylselenide (BnSeCF₃) 708, 709
 - β-aminoethane sulfonamides 649
 - β-arylethenesulfonyl fluorides 641–642, 647–649, 653–655
 - β,β-diarylenals 394
 - β-bromo-α,β-unsaturated ketones 701
 - β-carbonyl difluoromethyl sulfoxides [RS(O)CF₂Y]
 - applications 502
 - preparation 500–502
 - β-fluoro-α-aminophosphonates 791
 - β-, γ-, δ- and ε-trifluoromethylthiolated ketones 409
 - β,γ-unsaturated oximes 70, 73, 110
 - β-haloalkyl-perfluorosulfanyl compounds
 - α-Pentafluorosulfanyl aldehydes 581–582
 - γ-SF₅-α,β-unsaturated aldehydes 586–588
 - halogen substitution reactions 580–581
 - SF₅-substituted C₂-building blocks
 - acetic acid derivatives 588–597
 - difluoro-pentafluorosulfanyl acetic acid (SF₅CF₂CO₂H) derivatives 597–599
 - SF₅CF₂CF₂X 599–601
 - vinyl-SF₅ compounds
 - cycloadditions of 585–586
 - hydrogen halogenides from β-halogen-pentafluorosulfanylalkanes 583–584
 - β-ketoesters 97, 101, 125–126, 276–277, 320, 324, 329, 331, 334, 336, 419, 421, 423, 428, 430–433, 455, 456, 458, 469–470, 778

- β -ketophosphonates 771
- β -sultams 648
- β -trifluoromethylthio-
trifluoromethylated
compounds 413
- bidentate $(\text{CF}_3)_2\text{P}$ ligand 768
- bifunctional squaramide-catalyzed
one-pot electrophilic
trifluoromethylthiolation/
sulfur–Michael/aldol cascade
reaction 423
- Billard reagents 325, 327
- Billard's trifluoromethanesulfenamide
reagents 441
- bioactive S-trifluoromethyl
sulfoximines 676
- biotin–PEG₃–azide 670
- 2,2'-bipyridine copper
trifluoromethylthiolate ((bpy)
CuSCF₃) 313–315
- bipyridyl ligand dtbpy
(4,4'-di-tert-butyl-2,2'-
bipyridine) 389
- bis-and tris(pentafluorosulfanyl)
benzenes 561
- bis-and tris(sulfur chlorotetrafluorides)
558, 560, 561
- 1,2-bis(alkynyl)arenes 384
- bis-cinchona alkaloid
organocatalyst 433
- 1,1'-bis(diphenylphosphino)ferrocene
(dppf) 6, 378, 703
- bis(fluoroalkyl)phosphine-oxazoline
ligands 768, 770
- bis(fluorosulfonyl)biarenes 649–650
- bis-(2-methoxyethyl) aminosulfur
trifluoride (deoxofluor[®]) 740
- bis(perfluoroalkyl)sulfur
oxydifluorides 680
- bis-SCF₃ allylic acids 407
- (bis)sulfilimines 683
- bis(sulfonyl)difluoromethanes 539
- bistrifluoromethyl disulfide
(CF₃SSCF₃) 309, 317, 404
- 1,2-bis(trifluoromethylthio)
ethane 375, 378
- 1,2-bis(trifluoromethyl)thiolation 350,
351
- bistrifluoromethyl peroxide
(BTMP) 208, 210, 239
- bis(trifluoromethyl) sulfoxide 219,
489–490
- bis(trifluoromethylthio)ketene 374, 375
- bis(trifluoromethylthio) mercury
Hg(SCF₃)₂ 309–310, 434
- bis(trifluoromethyl) trioxide 208,
210–211
- bis(triflyl)methanide 518
- bis(triphenylphosphine) ligated
CuSCF₃ 439
- [bmim][SCF₃] 435
- Borodin–Hunsdiecker reaction 530
- boronic acids 26, 59, 131, 228, 281,
320, 323–324, 334, 343, 352–354,
368, 387–389, 430, 458, 460,
463–464, 480, 526, 538, 650–651,
653, 661–663, 704, 706, 711, 776,
778
- boron-mediated Mukaiyama aldol
reaction
chiral auxiliary, SF₅-acetate 597
of octyl SF₅-acetate with
aldehydes 595, 596
- BrCF₂CH=CH₂ 89–93
- BrCF₂CO₂Et 11, 31, 37, 38, 49, 66–70,
74, 79, 89–90, 104–106, 270,
469, 731
- BrCF₂P(O)(OR)₂ 49, 56, 59, 774–777
- bromo-and iododifluoromethane 726
- bromoarenes 362
- bromobenzo[d]thiazoles 363
(bromodifluoromethyl)
triphenylphosphonium
bromide 779
- bromodifluoromethyl aryl
sulfones 529, 531
- bromodifluoromethylphosphonates
271, 774–777, 788
substrate scope 60
- bromodifluoromethyl sulfones 530, 532
- bromodifluoromethyl
thioethers 292–293

- bromo-2-fluoroethane 574
- bromimidazo[1,2-*a*]pyrazines 363
- bromimidazoles 363
- bromooxazoles 363
- bromopentafluorosulfanylation 574
- 1-bromo-2-(pentafluorosulfanyl)ethane 574
- 2-bromo-1-pentafluorosulfanyl propionates 581
- 1-bromo-2-phenylacetylene 378
- 3-bromopyridines 363, 699
- 4-bromopyridines 699
- bromopyridines 362, 651
- bromopyrimidines 363
- bromoquinolines 362
- bromoquinoxalines 363
- Brønsted acid 65
- Buchwald–Hartwig aminations
 - aryl fluorosulfates and aniline 664, 666
- Buchwald–Hartwig reactions 354
- Bunte salt $\text{FCH}_2\text{SSO}_3\text{Na}$ 465
- C**
- calcium bistriflimide– $\text{Ca}(\text{NTf}_2)_2$ 643
- carbon-centered nucleophiles 518
- 1,1'-carbonyldiimidazole 120
- carboxylation of aryl
 - fluorosulfates 664
- carboxylic acids 70, 100, 119, 126–127, 152, 178–180, 242, 278, 294, 357, 392, 396, 408–412, 458, 473, 535, 578, 580, 582, 588, 591, 613–614, 664–665, 742, 754–756, 778, 781–783, 785, 797
- carfentrazone-ethyl 726
- catalytic metal-difluorocarbene
 - involved coupling (MeDIC) reaction 3, 10–11
- catalytic Togni's/Umemoto's reagent 512
- catalyzed nucleophilic, aromatics 3
- Cbz-protected
 - α -ketiminophosphonate 787
- $\text{C}=\text{C}$ double bonds
 - difluoromethylation rearrangements 73–76
 - subsequent cyclization 69–73
 - intermolecular difunctionalization
 - $\text{BrCF}_2\text{CO}_2\text{Et}$ 66–68
 - $\text{BrCF}_2\text{P}(\text{O})(\text{OR})_2$ 56–59
 - HCF_2R ($\text{R} = \text{CO}_2\text{H}$, $\text{SO}_2\text{NHNHBoc}$) 62–64
 - $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$ 59–62
 - selectfluor 65–66
- 1-*C*-diethylphosphono(difluoromethyl) iminosugars 774
- cefazaflur 291
- cesium trifluoromethylthiolates
 - (CsSCF_3) 315–316, 434, 439
- CF_2Br_2 97, 145–149, 153–155, 292, 716, 743–747, 779
- CF_2Br_2 , CF_2BrCl 102–103
- $\text{CF}_2\text{PO}(\text{OEt})_2$ group 465, 468, 779
- CF_2R moiety
 - organic substrates 49
 - synthetic pathways 49
- CF_3Br 297–301
- (3- CF_3)BzOO*t*-Bu 408
- (CF_3CO_2) $_2$ Xe 301–302
- CF_3COONa 152
- CF_3COSR 301
- CF_3 -donor reagents 297
- $\text{CF}_3\text{I}/\text{Na}/\text{liq. NH}_3$ system 298
- CF_3S -containing spiro-cyclopentanone–thiochromanes 423
- CF_3SeCl generation–trifluoromethylselenolation 709
- CF_3SeCu –DMF complex 697
- CF_3Se moiety
 - benzyltrifluoromethylselenide 708–710
- $\text{CF}_3\text{SeNMe}_4$ 711–712
- difluoromethylselenyl motif 714–715
- FG- CF_2Se -molecules 715–716
- fluoromethylselenyl motif 715
- higher fluorinated
 - homologues 713–714
- in situ* combination of
 - trifluoromethylation and elemental selenium 705–706

- CF_3Se moiety (*Contd.*)
 nucleophilic
 trifluoromethylation 694–695
 radical
 trifluoromethylation 695–696
 radical trifluoromethylselenolation
 712–713
 tetramethylammonium
 trifluoromethylselenolate
 ($\text{Me}_4\text{NSeCF}_3$) 701–705
 trifluoromethylseleno-
 copper 697–701
 trifluoromethylselenotoluene
 sulfonate (CF_3SeTs) 707,
 710–711
 trifluoromethylselenyl
 chloride 707–708
 $\text{CF}_3\text{SeNMe}_4$ 711–712
 $\text{CF}_3\text{SO}_2\text{Na}$ 300–301, 312, 334–337,
 346–347, 353, 356, 360–361, 417,
 743
 $(\text{CF}_3\text{SO}_2)_2\text{O}$ -promoted reduction 304
 $\text{CF}_3\text{SO}_2\text{SR}$ 301
 CF_3S -oxindoles 433
 CF_3 -substituted organometallic
 derivatives 164–169
 CF_3X ($\text{X}=\text{H}, \text{I}, \text{TMS}$) reagents 99
 C–H bond difluoroalkylation,
 DAAS-Na 31, 33, 41
 CH_2FBr 131
 CH_2FI 124, 125, 130–131
 $\text{CH}_2\text{FSO}_2\text{Cl}$ 128–129
 CH_2FX ($\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{OTf}, \text{OTs},$
 OMs) 125
 chiral α -amino acid-derived
 aldehydes 772
 chiral diphosphine ligand (*R*)-(2'-
 (bis(trifluoromethyl)
 phosphino)-1,1'-binaphthyl-2-yl)
 diphenylphosphine 766
 chiral enantiopure N- SCF_3
 reagents 331
 chiral fluorinated aminophosphonic
 acid derivatives
 difluoromethylated
 aminophosphonate
 derivatives 787–788
 monofluoroalkylated
 aminophosphonate
 derivatives 788–792
 trifluoromethylated
 aminophosphonate
 derivatives 785–787
 chiral fluoro-organo
 phosphines 765–770
 chiral trifluoromethyl substituted
 dithioketals 322
 chiral trifluoromethylthiolated 2,5-
 disubstituted oxazolines 428
 2-chloro-or 2-bromo-1-
 (trifluoromethylthio)
 alkanes 374
 chlorodifluoromethyl aryl sulfone 271,
 531
 chlorodifluoromethyl phenyl
 sulfone 530, 733–735
 1-(chloromethyl)-4-fluoro-1,4-
 diazoniabicyclo[2.2.2]octane
 salt 65
 chloropentafluorosulfanylation
 reactions 577
 2-(chlorotetrafluorosulfanyl)
 pyridines 562
 1-chloro-2-(trifluoromethylthio)
 alkenes 384
 2-chloro-3-(trifluoromethylthio)-1*H*-
 indole 303
 chloroxyperfluoroalkanes 209
 cinchona alkaloid-catalyzed
 enantioselective
 trifluoromethylthiolation 421
 cinnamic acids 392, 408, 417
cis-trifluoromethoxypalladation
 (FOP) 255
 $\text{ClCF}_2\text{COONa}$ 149–152, 155, 165
 cobalt-catalyzed cross-coupling 33
 bromodifluoroacetates 37
 Co(III)-catalyzed hydro-
 difluoromethylthiolation
 reaction 458
 complex (bpy) CuSCF_3 314–315
 copper-assisted oxidative bis-
 trifluoromethylthiolation 407
 copper-catalyzed cross-coupling

- α -silyldifluoroamides 29
- bromozinc-difluorophosphonate 25
- bromozinc-difluorophosphonate with
2-iodobenzoates 24
- iodo/bromo-aryl triazenes 25
- copper-catalyzed difluoroacetylation
bromodifluoroacetates 30
- copper-catalyzed difluoromethylation
(DMPU)₂Zn(CF₂H)₂ 9
- copper-catalyzed
phosphonyldifluoromethylation
(hetero)aryl iodides 28
- copper-catalyzed ring-opening
trifluoromethylthiolation of
cyclopropanols 415
- copper-catalyzed
trifluoromethylselenolation
704, 705
- copper-catalyzed
trifluoromethylthiolation 430
of vinyl iodides 379
- copper-free electrophilic method 391
- copper(I)-catalyzed
oxydifluoroalkylation of
alkenes 72
- copper(I) (phenylsulfonyl)
difluoromethide 526
- copper(I) trifluoromethylselenolate
complexes 697, 698
- copper(I) trifluoromethylthiolate
(CuSCF₃) 313, 405, 438, 697
- copper-mediated difluoromethylation
aryl iodides, TMSCF₂H 4
(hetero)arenediazoniums 5
heteroarenes 6
n-Bu₃SnCF₂H 5
- copper-mediated oxidative
phosphonyldifluoromethylation
TMSCF₂PO(OEt)₂ 28
- copper-mediated oxidative
trifluoromethylthiolation
reactions 392
- copper-mediated
phosphonyldifluoromethylation
aryl hypervalent iodides 28
difluoromethylphosphonyl cadmium\
zinc reagents 23
- copper (phenylsulfonyl)
difluoromethide 538
- copper triflate (CuOTf) 237, 682, 705
- copper trifluoromethylthiolate
(CuSCF₃) 312, 313, 437–439
- coumarin-3-carboxylic acid
substrates 392
- C-radical precursors 415
- C-SCF₂PO(OEt)₂ 466
- C(sp³)-centered electrophiles 537
- C(sp³)-CF₂PO(OEt)₂ bonds 56
- C(sp³)-SCF₃ compounds
direct construction of alkyl
trifluoromethyl sulfides 403
electrophilic trifluoromethylthiolation
reagents 418
via formation of F₃CS'
radical 415–417
- N*-trifluoromethanesulfenamides
419
- N*-trifluoromethylthiodi-
benzenesulfonimide
(PhSO₂)₂NSCF₃ 425–428
- N*-trifluoromethylthiophtha-
limide 419–423
- N*-trifluoromethylthiosaccharin
423–425
- N*-trifluoromethylthiosucc-
inimide 419–423
- nucleophilic
trifluoromethylthiolation
434–443
- O-SCF₃ reagents 428–431
- photochemical radical
trifluoromethylthiolation under
UV irradiation 404–405
- via pre-formation of R'
radical 411–415
- radical trifluoromethylthiolation with
the aid of anionic SCF₃
reagents 405–411
- silver trifluoromethylthiolate
AgSCF₃ 433
- (1S)-(-)-*N*-trifluoromethylthio-2,10-
camphorsultam 428
- trifluoromethanesulfonyl chloride
(CF₃SO₂Cl) 432

- $C(sp^3)$ -SCF₃ compounds (*Contd.*)
 trifluoromethanesulfonyl diazo reagent 432
 trifluoromethanesulfonyl hypervalent iodonium ylide 431–432
 trifluoromethyl diethylaminosulfur difluoride (CF₃-DAST) 432–433
 CuCF₂PO(OEt)₂ reagent 466, 468
 4-cyano-*N*-trifluoromethoxypyridinium triflimide 213, 214
 cyanotrifluoromethylthiolated compounds 407
 cycloalkadienes 576, 601
 cycloalkanols 409–410, 415–416, 462
 cycloalkenes 576
 cyclohexa-1,4-dienes 604
 cyclohexenyl
 trifluoromethylthioethers 393
 cyclopropanation 152, 157, 160, 177, 180, 772, 788
 1,1-difluoroalkenes 138, 142–143
 cyclopropane ring 135, 137, 157–158, 173
 CYP17A1 752
- d**
- decarboxylative difluorocarbene generation
 difluorocyclopropyl anion 150
 gem-difluorocyclopropyl, organoboron 151
 methylenecyclopropanes 150
 Ph₃P⁺CF₂CO₂[−] (PDFA) 153
 proline derived enecarbamate 151
 reagents for 149
 decarboxylative fluorination 197, 199–200, 269, 272, 278–279, 285, 292–293
 decarboxylative reactions 728–733
 dehydroxytrifluoromethylthiolation protocol 437
 δ-sultones 647–649
 demethylthiolative fluorination 279–280
 density functional theory (DFT) 100, 171–172, 231, 239, 243–244, 255, 379, 579, 591
 deoxyfluorination, fluoroformates 198
 deoxytrifluoromethylthiolation approach 381
 Dess Martin periodinane reagent 701
 dialkylsulfamoyl fluorides 633, 635, 638, 669
 1,1-diaryl-2,2-difluoroethene 302
 2,2-diaryl-1,1-difluoroethenes 526
 diaryl selenide 425
 1,1-diaryl-2,2,2-trifluoroethanethiol 302
 diaryl trifluoromethyl sulfonium salts 293, 481–482
 diastereomerically pure SCF₃-substituted enamine products 382
 dibromodichloromethane 405
 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) 255
 1,3-dibromo-5,5-dimethylhydantoin (DBH) 198, 741
 1,2-dibromoethane 378, 518
 dicationic imidazolium-phosphonium salt [(SImes)PFPh₂] [B(C₆F₅)₄]₂ 797
 1,1-dichlorocyclopropanes 140–142
 1,1-dichlorocycloproparene 142
 Diels–Alder reaction
 acrylic acid derivatives 590
 cyclopentadiene 585
 SF₅-acetylenes 604–605
 SF₅-benzyne 569
 2-SF₅-butadiene 586
 SF₅-substituted acroleine 585
 diethyl
 α-amino-α-trifluoromethyl-γ-oxobutylphosphonates 787
 diethyl
 α-fluoro-β-ketophosphonates 771
 diethylaminosulfur trifluoride (DAST) 3, 23, 47, 274, 280, 325, 419, 432–433, 538, 740–741, 788, 791
 diethyl bromodifluoromethylphosphonate ((EtO)₂P(O)CF₂Br) 774

- diethyl (difluoromethyl)
 - phosphonate 773–774
- diethylisopropylamine (DIPEA)
 - 631–632, 659–660
- diethyl trifluoromethyl-
 - phosphonate 297, 694, 784–785
- 1,1-difluorination of styrenes 66, 68
- difluorination reaction 67
- 6-difluoroacetate phenanthridines 78
- 1,1-difluoroalkenes,
 - cyclopropanation 142
- difluoroalkylated indolino-3-ones 82
- 1-difluoroalkylated isoquinolines 76, 80
- difluoroalkylation
 - electrophilic
 - CF_3X ($\text{X} = \text{H}, \text{I}, \text{TMS}$)
 - reagents 99–100
 - free radical
 - halodifluoroketone
 - or-amide 107
 - HCF_2I and $\text{PhCH}_2\text{CF}_2\text{I}$ 107–108
 - iododifluoroacetates 101–102
 - (hetero)aromatics
 - catalytic difluoroalkylation
 - 37–39
 - transition-metal catalyzed
 - difluoroacetylation 27–33
 - transition-metal catalyzed
 - phosphonyl 23–26
 - nucleophilic
 - $\text{BrCF}_2\text{CO}_2\text{Et}$ and $\text{BrCF}_2\text{CH}=\text{CH}_2$ 89–90
 - silanes 94–95
 - $\text{XCF}_2\text{PO}(\text{OEt})_2$ 89
 - $\text{XCF}_2\text{SO}_2\text{Ar}$ 90–93
- difluorocarbene 10–11, 149–163, 731
 - $\text{BrCF}_2\text{CO}_2\text{H}$ 270
 - $\text{BrCF}_2\text{P}(\text{O})(\text{OEt})_2$ 271
 - chlorodifluoromethyl aryl
 - ketones 272
 - Cu-complex 269–272
 - $\text{FSO}_2\text{CF}_2\text{CO}_2\text{H}$ 270
 - O–H bond 269
 - $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$ 269
 - reagents 97–99
 - TMSCF_2Br 271
- difluorocarbene donor reagent
 - $(\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-;$
 - PDFA) 270–271, 439, 733
- difluorocyclopropanation
 - AuCF_3 complexes 170
 - $\text{Bi}(\text{CF}_3)_3$ 169
 - boc-protected amino
 - derivatives 161
 - CF_2Br_2 146–149
 - $(\text{CF}_3)_2\text{Cd}$ 168
 - $(\text{CF}_3)_2\text{Hg}/\text{NaI}$ 167
 - $\text{CF}_3\text{SiMe}_3/\text{NaI}$ system 179
 - CF_3SiMe_3 178
 - $(\text{CF}_3)_2\text{Zn}\cdot 2\text{DMPU}$ 168
 - enolizable ketones with TFDA 162
 - hexafluoropropene oxide 183
 - $\text{Me}_3\text{SnCF}_3/\text{NaI}$ 164
 - n*-butyl acrylate 177
 - N*-vinylazoles 181
 - $\text{PhHgCF}_3/(\text{CF}_3)_2\text{Hg}/\text{NaI}$ 167
 - $\text{PhHgCF}_3/\text{NaI}$ 166
 - $\text{Ph}_3\text{P}^+\text{CF}_2\text{Br Br}^-$ 154
 - phthalimide moiety 160
 - silyl enolates 174
 - tertiary amino function 161
- difluorocyclopropanation reagent
 - of alkene 143–145
 - $\text{BrCF}_2\text{P}(\text{O})(\text{OEt})_2$ 163
 - CF_2Br_2 with Zn 146–149
 - CF_3 -substituted organometallic
 - derivatives 164–169
 - decarboxylative difluorocarbene
 - generation 149–153
 - difluorodiazirine 182–183
 - double bond reactions 185–187
 - hexafluoropropene oxide 183
 - Michael-induced ring
 - closure 183–185
 - nucleophilic cleavage 153–163
 - Ruppert–Prakash-type
 - reagents 169–182
 - trihalomethyl anions CF_2X^- ($\text{X} = \text{Cl}, \text{Br}$) 145–146
- difluorocyclopropanes 728
- 2,2-difluorocyclopropyl
 - ketones 157–158

- 3,3-difluoro-3*H*-diazirine (DFD) 182–183
- difluorohomologation
 - carbonyl compounds 173
 - ketones 172
- 1,1-difluoro-2-
 - hydroxyalkylphosphates 89
- difluoromethanesulfonyl chloride ($\text{HCF}_2\text{SO}_2\text{Cl}$) 455
- difluoromethoxylation 269, 273–275, 285
- difluoromethyl aryl ethers 274, 530, 775
- difluoromethylated aminophosphonate derivatives 787–788
- difluoromethylated isoxazolines 70, 110
- difluoromethylated ketones 68
- difluoromethylation
 - alkynes 79–82, 85
 - C=C double bonds
 - intermolecular
 - difunctionalization 56–68
 - rearrangements 73–76
 - subsequent cyclization 69–73
 - electrophilic
 - difluorocarbene reagents 97–99
 - I(III)- $\text{CF}_2\text{SO}_2\text{Ph}$ reagent 100
 - S*-((phenylsulfonyl)difluoromethyl) thiophenium salts 100–101
 - free radical
 - CF_2Br_2 , CF_2BrCl or TMSCF_2Br 102–103
 - $\text{HCF}_2\text{SO}_2\text{Cl}$ and $\text{HCF}_2\text{SO}_2\text{Na/Zn}$ ($\text{SO}_2\text{CF}_2\text{H}$)₂ 108–109
 - phosphorus-containing reagents 103–104
 - sulfones, sulfoximines, thioethers and sulfonium salts 109–111
 - (hetero)aromatics
 - MeDIC 10–11
 - radical C–H bond 19–22
 - transition-metal catalyzed radical difluoromethylation 12–19
 - transition-metal mediated 3–10
 - isocyanides 76
 - nucleophilic
 - cadmium, copper and zinc reagents 90
 - miscellaneous reagents 96–97
 - $\text{PhSO}_2\text{CF}_2\text{H}$ 90–93
 - reagents 94–95
 - sulfoximine reagent 96
- difluoromethylcadmium 90, 91
- difluoromethylcopper 90
- difluoromethyl coumarins 527
- difluoromethyldiarylsulfoniums 733
- difluoro(methylene)cyclopropanes (F_2MCPs) 158
- difluoromethylene
 - phosphobetaine 731, 743, 779, 781–784
- 6-difluoromethylenephosphonyl-phenanthridines 776
- difluoromethylene ylides 781–782
- difluoromethyl phenyl sulfone ($\text{PhSO}_2\text{CF}_2\text{H}$) 90, 530
- difluoromethyl-phosphonium bromide 779
- difluoromethylphosphonium salts 103, 779, 781–783
- difluoromethyl 2-pyridyl sulfone 19, 93, 522
- difluoromethylselenoethers 714
- difluoromethylselenyl motif 714–715
- 1,1-difluoro-1-(methylsulfinyl) alkanes 502
- difluoromethyl sulfones [$\text{RSO}_2\text{CF}_2\text{H}$]
 - aryl and heteroaryl difluoromethyl sulfones 520–529
 - aryl and heteroaryl
 - halodifluoromethyl sulfones 529–535
 - aryl (trimethylsilyl)difluoromethyl sulfones 536–538
 - other (miscellaneous) aryl
 - difluoromethyl sulfones 539–540
- difluoromethyl sulfoxides ($\text{RS(O)CF}_2\text{R}$)
 - applications 494–498
 - preparation 493–494, 502–504
 - and uses 502–504
- 2-(difluoromethylsulfonyl) benzothiazole 527, 529

- difluoromethylthioester
 derivatives 460
 difluoromethylthiolation reaction
 electrophilic reagents 453–457
 by nucleophilic pathway 453
 PhSO₂SCF₂H 457–462
 difluoro-pentafluorosulfanyl acetic acid
 (SF₅CF₂CO₂H)
 derivatives 597–599
 difluoro(trimethylsilyl)
 methylphosphonates 777–778
 di(hetero)aryl-λ³-iodanes 357–358
 dihydroisoquinolinones 709
 (1,1-dihydrotrifluoroethyl)
 phenyliodonium triflate 754
 diiodomethane 405
 diisopropylethylamine (DIPEA) 631,
 659, 660
 dimeric selenolated complexes 698
 1,3-dimesitylimidazol-2-ylidene
 (IMes) 162
 1,2-dimethoxyethane (DME) 154–155,
 164–165, 397, 750
 dimethoxy-substituted chiral
 sulfonamide reagent 428
 dimethylacetamide (DMA) 59
 1,3-dimethylbenzene 344
 2,4-dimethylbenzenesulfonyl
 (DMPs) 254
 dimethylformamide (DMF) 59, 491
 1,3-dimethyl-2-imidazolidinone
 (DMI) 184
 5,5-dimethyl-1-pyrroline *N*-oxide
 (DMPO) 246
 dinitrophenyl disulfides 554, 556
 2,4-dinitro (trifluoromethoxy)benzene
 (DNTFB) 221
 diphenyl disulfide 506, 554
 silver difluoride (AgF₂) 552
 2,2'-dipyridyl disulfide 553, 562
 direct anionic trifluoromethoxylation
 aryl stannanes and arylboronic
 acids 230
 deoxytrifluoromethoxylation of
 phenols 228
 N-(hetero)
 aryl-*N*-hydroxylamines 230
 nucleophilic reactions 229
 ortho-trifluoromethoxylated
 anilide 232
 Stern–Volmer quenching 232, 235
 trifluoromethyl benzoate 236
 direct C–H functionalization 343
 direct electrophilic
 difluoromethylation 269,
 272–273
 direct radical trifluoromethoxylation
 CF₃OO CF₃ 239
 C–H trifluoromethoxylation 243
 C–H trifluoromethoxylation of
 arenes 247
 CW-EPR studies 248
 heteroaryl trifluoromethyl
 ethers 249
 N-trifluoromethoxy pyridine
 salts 242
 Ru(bpy)₃²⁺ 245
 trifluoromethoxyl radical 239
 direct trifluoromethoxylation
 sp³-carbon atoms
 alkyl alcohols and alkyl
 silanes 259–260
 alkyl halides and alkyl
 triflates 258
 α-diazo esters 263–264
 C–H bonds 260–262
 of epoxides 262–263
 direct trifluoromethoxylation of alkenes
 Pd(II)-catalyzed oxidative 252–255
 radical
 trifluoromethoxylation 251–252
 silver(I)-catalyzed 255–257
 direct trifluoromethoxylation reagents
 bistrifluoromethyl peroxide 210
 bis(trifluoromethyl)
 trioxide 210–211
 chloroxyperfluoroalkanes 209
 2,4-dinitro (trifluoromethoxy)
 benzene 221
 N-trifluoromethoxy
 benzimidazole 211–212
 N-trifluoromethoxysaccharin 213
 N-trifluoromethoxy triazolium
 salts 214–215

direct trifluoromethoxylation reagents
(*Contd.*)

organometallic

trifluoromethoxides 217–219

perfluoroalkylsulfurane 219

perfluoroalkylsulfurane

oxide 219–220

trifluoromethyl benzoate 222–223

trifluoromethyl

hypofluorite 207–209

trifluoromethyl sulfonates 221–222

trifluoromethyl

trifluoromethane-

sulfonate 215–217

direct trifluoromethylation, OCF₃

motif 200

di-*t*-butyl azodicarboxylate 750

Doyle–Kirmse rearrangement 469,
472

dtbbpy 17, 70, 76, 79

e

EAS-type ^{het}ArS(O)CF₃ synthesis 486

EAS-type triflinyl heteroarene

synthesis 485

(*E*)-1,2-bis(trifluoromethylthio)

alkenes 384, 396

electron paramagnetic resonance

(EPR) 12, 246, 248

electron-rich (hetero)arenes 317

electrophilic difluoroalkylation 37,
100

CF₃X (X = H, I, TMS) reagents 99

electrophilic difluoromethylating

reagents 48, 100, 736

electrophilic difluoromethylation

difluorocarbene reagents 97–99

I(III)-CF₂SO₂Ph reagent 100

S-((phenylsulfonyl)difluoromethyl)

thiophenium salts 100–101

electrophilic difluoromethylsulfonyl

chloride (HCF₂SCI) 455

electrophilic fluorophosphonium

cation 793

electrophilic hypervalent iodine

reagent 428

electrophilic monofluoromethylation

CH₂FX (X = Cl, Br, I, OTf, OTs,
OMs) 125

monofluoromethyl phosphonium

salts 127

monofluoromethylsulfonium

ylides 127

monofluoromethylsulfoxinium

salts 126

S-(monofluoromethyl)

diarylsulfonium

tetrafluoroborate 125–126

of thiophenol 463

electrophilic (PhSO₂)₂NSCF₃

reagent 425

electrophilic SCF₃ reagent *N*-

(trifluoromethylthio)

pyrrolidine-2,5-dione 416

electrophilic trifluoroethyl

sources 753–756

electrophilic trifluoromethylation 200,

207, 259, 302–303, 351, 376, 419,

482, 681, 743–750

of thiolates or thiols 291, 293–294

electrophilic trifluoromethylthiolating

reagent *N*-(trifluoromethylthio)

phthalimide 344, 384, 391

electrophilic trifluoromethylthiolation

381–391, 403, 488

electrophilic trifluoromethylthiolation

reagents 418–433

Billard reagents 325–327

bistrifluoromethyl disulfide

(CF₃SSSCF₃) 317

chiral enantiopure *N*-SCF₃

reagents 331

Haas reagents 318–319

Lu–Shen reagents 319–321

N-(trifluoromethylthio)-

bis(phenylsulfonyl)

imide 329–331

N-(trifluoromethylthio)

phthalimide 323–325

N-trifluoromethylthio-

saccharin 328–329

N-trifluoromethylthiosuccinimide

322–323

Shibata's reagent 331–334

- sodium trifluoromethanesulfonate
 ($\text{CF}_3\text{SO}_2\text{Na}$) 334
 trifluoromethanesulfonyl chloride
 (CF_3SOCl) 317
 trifluoromethanesulfinyl chloride
 (CF_3SOCl) 335–337
 trifluoromethanesulfonyl chloride
 ($\text{CF}_3\text{SO}_2\text{Cl}$) 334–335
 electrophilic-type
 trifluoromethylation 507
 elemental fluorine 517, 554–558,
 571
 employing Billard's sulfenamide
 reagent *N*-phenyl-*S*-
 (trifluoromethyl)
 thiohydroxylamine 384
 enamines 65, 165, 167, 317, 324, 333,
 357, 382–383, 419, 421, 456, 537,
 751, 778
 enantiomerically pure α - SCF_3 -
 substituted alcohols 119, 421
 enantiomerically pure
 (*S*)-2,2'-binaphthol 766
 enantiomerically pure *S*- R_F
 sulfoximines 680
 enantiopure α,α -difluoro- β -
 aminophosphonic acids 787
 enantiopure β -trifluoromethylthiolated
 ketoesters 421
 enantiopure *N*- SCF_3 reagents 331,
 332
 enantioselective proline-catalyzed
 Mannich reaction 786–787
 endothelin (ET-1) receptor
 antagonists 662–663, 732
 1,6-enynes 101, 394, 395
 ethenesulfonyl fluoride (ESF)
 derivatives 647–649, 652–655
 [(ethoxycarbonyl)difluoromethyl]thio]
 phthalimide 469
 ethyl 2-difluoro-2-(arylsulfinyl)
 acetates 2, 502
 ethyl 4-(phenylamino)benzoate 665
 ethyl bromodifluoroacetate 728
 ethyl iododifluoroacetate 406
 Evans-type chiral lithium imide
 enolates 421
- f**
 [^{18}F] CF_3SePh 694
 $\text{F}_3\text{COOOCF}_3$ reactivity 211
 FDA 47, 48
 difluoromethyl group 48
 Fe_2O_3 -promoted
 trifluoromethylthiolation of
 alkenes 414
 ferroelectric liquid crystals 137, 155
 FG- CF_2Se -molecules 716
 Fischer carbene-type 177
 ^{18}F -labeled trifluoromethyl
 thioethers 292
 fluorinated cyclic analogs (FAP4) 788,
 790, 791
 fluorinated
 cyclopropylphosphonates 772
 fluorinated *meta*- SF_5 -pyridines 563
 fluorinated *para*- SF_5 -pyridines 563
 fluorination 140–142, 197–200, 272,
 274–275, 278–280, 292–293,
 679–680, 739–743
 fluorination by bromine
 trifluoride 742
 fluorine/halogen exchange 739
 fluoroalkylation 11, 42, 110, 122, 477,
 496, 499, 524, 527, 531–532, 536,
 659–660
 fluorobenzenesulfonimide (NFSI) 272,
 329, 628
 2-fluoro-1,3-benzodithiole-1,1,3,3-
 tetraoxide (FBDT) 123
 6'-fluoro[4.3.0]bicyclonucleotides
 ($6'\text{F-bc}^{4,3}\text{-DNA}$) 173
 fluorobis(phenylsulfonyl)
 methane 121–122
 fluoroform 99, 295, 297, 506, 513,
 640–641, 694, 726, 730
 fluoroformates,
 deoxyfluorination 198
 fluoroform-derived CuCF_3 297
 fluoromalonates 119–120
 fluoromethylated spiro[5.5]
 trienone 83
 fluoromethyl phenyl sulfone 119–120
 fluoromethyl phenyl sulfoximine 681
 fluoromethylselenenyl motif 715

- 2-fluoro-1-(pentafluorosulfanyl) benzene 569
- 2-fluoro-2-phenylsulfonylacetophenone 122
- fluorophosphonium and fluoroalkylphosphonium cations 765, 793–801
- fluorosulfate-L-tyrosine (FSY) 668–669
- fluorosulfate moiety ($-\text{OSO}_2\text{F}$) 656, 662, 668
- fluorosulfates
- advantage of 656
 - C–F bond formation 658–659
 - C–N bond formation 659, 664–665
 - dehydration/ dehydrogenation 659–660
 - sulfur-fluoride exchange (SuFEx) chemistry 665–668
 - transition metal-catalyzed cross-coupling reactions
 - C–C bond formation 660–663
 - C–H bond formation 665
 - CO or CO_2 insertion 663–664
- fluorosulfonyldifluoroacetic acid 149, 152, 153, 155, 731–732
- (fluorosulfonyl)difluoromethyl sulfoxides 506
- 2-fluoro-2-sulfonylketone 122–123
- fluorosulfurylation 625, 628, 630–631, 633–638, 651, 662, 664–665
- free radical difluoroalkylation
- halodifluoroketone or-amide 107
 - HCF_2I and $\text{PhCH}_2\text{CF}_2\text{I}$ 107–108
 - iododifluoroacetates 101–102
- free radical difluoromethylation
- $\text{ArCF}_2\text{CO}_2\text{H}$ 112
 - CF_2Br_2 , CF_2BrCl or TMSCF_2Br 102
 - $\text{HCF}_2\text{SO}_2\text{Cl}$ and $\text{HCF}_2\text{SO}_2\text{Na/Zn}$ ($\text{SO}_2\text{CF}_2\text{H}$)₂ 108–109
 - phosphorus-containing reagents 103
 - sulfones, sulfoximines, thioethers and sulfonium salts 109–111
 - $\text{TMSCF}_2\text{CO}_2\text{Et}$ 112
- free radical hydrodifluoroalkylation
- $\text{BrCF}_2\text{CO}_2\text{Et}$ 104–106
 - halodifluoroketone or-amide 107
- free radical monofluoromethylation
- $\text{CH}_2\text{FSO}_2\text{Cl}$ 128–129
 - $(\text{H}_2\text{FCSO}_2)_2\text{Zn}$ (MFMS) 128
 - monofluoromethyl sulfone 130
 - $(\text{PhSO}_2)_2\text{CFI}$ 128
 - $\text{PhSO}(\text{NTs})\text{CH}_2\text{F}$ 129
- Freon 22 726
- Freund reaction 138, 140
- Friedel–Crafts-type direct trifluoromethylthiolation 335
- 5- ^{18}F -(trifluoromethyl) dibenzothiophenium trifluoromethanesulfonate 294
- ^{18}F]trifluoromethylthiolation 441, 783
- ^{18}F -Umemoto reagent 294
- furans 29, 30, 358, 364–365, 569
- g**
- γ -butenolides 396
- γ -fluoroalcohols 129
- gem*-difluorinated spiro- γ -lactam oxindoles 70, 72
- gem*-difluoroalkene 142, 143, 523, 527, 531, 781
- intramolecular cyclopropanation 143
- gem*-difluorocyclopropanes 656
- biological active 136
- cyclopropanation
- 1,1-difluoroalkenes 142–143
- difluorocyclopropanation reagents
- CF_2Br_2 with Zn 146–149
 - CF_3 -substituted organometallic derivatives 164–169
- decarboxylative difluorocarbene generation 149–153
- difluorodiazirine 182–183
- double bond reactions 185–187
- hexafluoropropene oxide 183
- Michael-induced ring closure (MIRC) 183–185
- nucleophilic cleavage 153–163
- Ruppert–Prakash-type reagents 169–182

- trihalomethyl anions CF_2X^- ($\text{X} = \text{Cl}, \text{Br}$) 145–146
 - drugs and natural products 136, 137
 - ferroelectric liquid crystals 137
 - gem*-difluoro moiety 138, 139
 - inducible T-cell kinase (ITK)
 - inhibitor 135
 - intramolecular Wurtz (Freund)
 - reaction 140
 - nucleophilic fluorination 140–142
 - $\text{Pd}^{(0)}$ -catalyzed ring opening 138
 - potential enzyme inhibitors 136
 - synthetic approaches 139
 - synthetic transformation of 138
 - gem*-difluoroolefins 99, 502, 541
 - gem*-difluoropropanes 657
 - $(i\text{-PrO})_2\text{P}(\text{O})\text{CBr}_2\text{F}$ 772
 - gem-disubstituted chloro
 - trifluoromethyl
 - compounds 336
 - global warming potential (GWP) 728
 - Grignard reagents 317, 321, 327, 350, 351, 366, 419, 504, 506, 508, 628, 709, 773
- h**
- Haas reagents 318, 319, 322
 - halazepam 752
 - halodifluoroketone/amide 107
 - halodifluoromethyl sulfoxides $[\text{RS}(\text{O})\text{CF}_2\text{X}]$
 - applications 499–500
 - preparation 498–499
 - haloforms reaction 145
 - halophilic reaction 146
 - Hansch constant 291
 - Hansch's hydrophobicity
 - parameter 309
 - Hantzsch ester (HE) 56, 185
 - Hass cyclopropane process 138
 - Hastelloy C 310
 - HCF_2I 90, 107–108
 - $\text{HCF}_2\text{P}(\text{O})(\text{OR})_2$ 773–774
 - HCF_2R ($\text{R} = \text{CO}_2\text{H}, \text{SO}_2\text{NHNHBoc}$) 62–64
 - $\text{HCF}_2\text{SO}_2\text{Cl}$ 108–109, 455, 456, 457
 - $\text{HCF}_2\text{SO}_2\text{Na}/\text{Zn}(\text{SO}_2\text{CF}_2\text{H})_2$ 108
 - Heck cross-coupling
 - reactions 652–653
 - hemiaminals 297, 694
 - (hetero)aromatic aldehydes 461
 - heteroaromatic compounds
 - furans 364–365
 - imidazo[1,2-*a*]pyridines 367
 - indoles 358–362
 - isoquinoline 362–364
 - Knochel–Hauser base 366
 - 1-phenyl-5-iodopyridinones 367
 - pyrazolin-5-ones 368
 - pyridine 362–364
 - pyrroles 358–362
 - quinoline 362–364
 - tetrafluoropyridazine 366
 - tetrafluoropyrimidine 366
 - thiophenes 364–365
 - (hetero)aromatics
 - difluoroalkylation
 - catalytic difluoroalkylation 33, 37–39
 - transition-metal catalyzed
 - phosphonyl 23–26
 - difluoromethylation
 - catalyzed nucleophilic 3–10
 - MeDIC 10–11
 - radical C–H bond 19–22
 - transition-metal catalyzed radical
 - difluoromethylation 12–19
 - transition-metal mediated 3–10
 - heteroaryl difluoromethyl
 - sulfones 520–529
 - heteroaryl triflones
 - preparation 513
 - uses 514
 - heteroaryl trifluoromethyl sulfoxides $[\text{hetArS}(\text{O})\text{CF}_3]$
 - applications 487–489
 - preparation 484–487
 - heterocyclic scaffolds 358
 - hexafluoroacetone hydrate amidinate
 - salt 297
 - hexafluoropropene oxide (HFPO) 145, 183
 - hexamethylphosphoramide (HMPA) 172, 393

- $(\text{H}_2\text{FCSO}_2)_2\text{Zn}$ (MFMS) 128
 higher fluorinated homologues 695, 696, 713–714
 Horner–Wadsworth–Emmons (HWE) olefination 582, 588, 772
 HOTf-promoted reduction of trifluoromethyl sulfoxides 305
 Huisgen alkyne–azide cycloaddition 660, 661
 Hu–Prakash protocol 175, 176
 hydrodifluoroalkylation 102
 of alkynes 82, 84
 hydrodifluoromethylation of alkenes 62, 63
 hydrophobictrifluoromethyl- λ^6 -tetrafluorosulfanyl (CF_3SF_4) group 613
 hydrophosphonodifluoromethylation 57
 plausible reaction pathway 58
 3-hydroxy-3-difluoroalkylisindolin-1-ones 66
 1,2-hydroxydifluoromethylation 64
 hypervalent iodine(III)– CF_3 reagents 293, 294
- i**
- I(III)– $\text{CF}_2\text{SO}_2\text{Ph}$ reagent 100
 imidazo[1,2-*a*]pyridines 367
 iminosulfur oxydifluorides 669–671
 2-imino-3,3,3-trifluoropropanephosphonates 785
 indanone-based β -ketoesters 455
 indirect trifluoromethylthiolation methods
 electrophilic trifluoromethylation of thiolates or thiols 293–294
 fluorination of polyhalogenalkyl thioethers 292–293
 nucleophilic trifluoromethylation 294–298
 radical trifluoromethylation 298–302
 reduction of trifluoromethyl sulfoxides 303–305
 trifluoromethylation of thiones/thioureas 302–303
- indoles 320, 333, 334, 336, 357–362, 367, 450, 455, 456, 459, 465, 469, 472, 487, 488, 504, 513, 749, 777, 778
 “innocent” oxidant 345
 in situ aromatic selenocyanates 694
in situ combination of trifluoromethylation and elemental selenium 705–706
in situ generated electrophilic species *N*-(trifluoromethylthio)succinimide 389
 interleukin-2 inducible T-cell kinase (ITK) inhibitor 135
 intermolecular difunctionalization
 $\text{BrCF}_2\text{CO}_2\text{Et}$ 66–68
 $\text{BrCF}_2\text{P}(\text{O})(\text{OR})_2$ 56–59
 HCF_2R ($\text{R}=\text{CO}_2\text{H}$, $\text{SO}_2\text{NHNHBoc}$) 62–64
 $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$ 59–62
 selectfluor 65–66
 internal styrene (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene 383
 intramolecular OCF_3 migration 202–203
 intramolecular trifluoromethylthiolation 407, 408
 intramolecular Wurtz (Freund) reaction 140
 iodine-free trifluoromethanesulfenate 321
 iodine pentafluoride 317, 563, 565, 567
 iodoalkyl triflones 520
 iododifluoroacetates 101–102
 iododifluoromethyl phenyl sulfone 530–531, 534
 iododifluoromethylsulfinylarenes 500
 iodo-isoxazoles 513
 iodoperfluoroalkyl phosphines 793
 3-iodopyrones 699
 Ireland–Claisen rearrangement 159
 carboxylic acid 614
 of SF_5 -acetic acid allyl esters 592
 of SF_5 -acetic acid cinnamyl esters 593

iron-catalyzed difluoroalkylation
 unactivated difluoroalkyl
 bromides 41
 iron-catalyzed difluoromethylation
 aryl magnesium reagents 20
 aryl zinc reagents 20
 iron-mediated
 hydrotrifluoromethylthiolation 412–413
 isochromenones 469, 709
 isocyanides,
 difluoromethylation 76–79
 isoindolin-1-ones 65
 isolated SCF_3 -substituted
 diarylalkenes 394
 isoquinoline 362, 709
 isoquinolinediones 362–364, 416,
 709
 isosteric (difluoromethyl)
 phosphonate 774

j

Johnson–Corey–Chaykovsky
 reaction 582
 Johnson-type sulfoximinium
 reagent 496

k

{K(18-crown-6)} $\text{P}(\text{CF}_3)_2$ 768
 Knochel–Hauser base 366
 Knochel–Hauser base-promoted
 reaction 366
 Kolomeitsev's method 234
 $\text{K}_2\text{S}_2\text{O}_8$ 261, 301, 336, 391, 393, 394,
 407, 408, 411, 414, 415, 460, 462

l

Langlois reagent 695, 743
 Langlois reagent $\text{CF}_3\text{SO}_2\text{Na}$ 312, 360
 Langlois reagent (NaSO_2CF_3) 382
 laser flash photolytic (LFP) 183
 Lewis acid–base adducts (LA-X) 622
 liquid crystalline alkenes 577
 lithium fluorocarbenoid (LiCH_2F) 124
 lithium 2-phenylpropan-2-olate 321
 L-phosphoallothreonine 788
 L-phosphoserine 788, 789

L-phosphothreonine 788
 Lu–Shen reagents 319–321, 353

m

MCF_3 complex 297, 298
 $\text{Me}_3\text{SiCF}_2\text{X}$ 169, 171
 mercaptans 292
 2-mercapto pyridine 522
 $\text{MesNHSCF}_2\text{P}(\text{O})(\text{OEt})_2$ 778, 779
 metabotropic glutamate receptor
 (mGluR) 135
 metal-catalyst-free
 trifluoromethylthiolation 349
 metal-difluorocarbene involved
 coupling (MeDIC) 3, 10–11, 42
 metal-free
 trifluoromethylthiolation 361
 metallaphotoredox difluoromethylation
 with bromodifluoromethane 17
 (methoxycarbonyl)
 difluoro-
 methanesulfonamide 469
 methoxymethyl (MOM) ethers 438
 3-(4-methoxyphenyl)propionic
 acid 392, 393
 1-methoxy-4-(1-propyn-1-yl)-
 benzene 462
 methyl chlorodifluoroacetate 153,
 728
 methylene cyclohexane 576
 methylenecyclopropylglycine
 (MCPG) 150
 methyl perfluorooctyl sulfoxide 677
 MFDA, difluorocarbene from 156
 Michael-induced ring closure
 (MIRC) 139, 183–185
 Michler's thioketone 376
 miscellaneous reagents 96, 97
 mono- and difluoromethyl
 sulfoximines 686
 mono- and difluoromethyl NH-
 sulfoximines 685
 monofluoroalkylated
 aminophosphonate
 derivatives 788–792
 monofluoromethanesulfinate
 (MFMS) 128

- monofluoromethylation 275
 - electrophilic
 - CH_2FX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OTf}, \text{OTs}, \text{OMs}$) 125
 - monofluoromethyl phosphonium
 - salts 127
 - monofluoromethylsulfonium
 - ylides 127
 - monofluoromethylsulfoxinium
 - salts 126
 - S*-(monofluoromethyl)
 - diarylsulfonium
 - tetrafluoroborate 125–126
 - free radical
 - $\text{CH}_2\text{FSO}_2\text{Cl}$ 128–129
 - $(\text{H}_2\text{FCO}_2)_2\text{Zn}$ (MFMS) 128
 - monofluoromethyl sulfone 130
 - $(\text{PhSO}_2)_2\text{CFI}$ 128
 - $\text{PhSO}(\text{NTs})\text{CH}_2\text{F}$ 129
 - nucleophilic
 - CH_2FI 124
 - 2-fluoro-1,3-benzodithiole-1,1,3,3-tetraoxide 123
 - fluorobis(phenylsulfonyl)
 - methane 121–122
 - fluoromalonates 119
 - fluoromethyl phenyl
 - sulfone 119–120
 - 2-fluoro-2-sulfonylketone 122
 - monofluoromethyl phosphonium
 - salts 124
 - $\text{PhSO}(\text{NTBS})\text{CH}_2\text{F}$ 123–124
 - $\text{TMSCF}(\text{SO}_2\text{Ph})_2$ (TFBSM) 123
 - transition-metal-catalyzed/mediated
 - CH_2FBr 131
 - CH_2FI 130–131
 - cross-coupling reactions 130
 - PhSO_2CHFI 131
 - $\text{PTSO}_2\text{CH}_2\text{F}$ 132
 - monofluoromethylation of thiols 463
 - monofluoromethylphosphonate
 - reagents 770–772
 - monofluoromethyl phosphonates 770
 - monofluoromethyl phosphonium
 - salts 124, 127
 - monofluoromethylselenoethers 715, 716
 - monofluoromethyl sulfone 130
 - monofluoromethylsulfonium
 - ylides 127
 - monofluoromethylsulfoxinium
 - salts 126
 - monofluoromethylthioesters 464
 - mono- or di-halocubanes 406
 - 2-monosubstituted 3-allenoic acids 2, 407
 - Morita–Baylis–Hillman (MBH)
 - alcohols 436
 - carbonates 442
 - Mukaiyama aldol product 592
 - Munavalli reagent 323

n

 - N*-acetyltyrosine 622
 - $\text{NaI}/(\text{CF}_3\text{CO})_2\text{O}$ 303
 - “naked fluoride” method 624
 - N*-alkenoxypyridinium 436
 - N*-alkylimidazoles 732
 - naphthalene 344
 - N*-arylacrylamides 108, 128, 407, 416
 - $\text{Na}_2\text{SO}_3/\text{HCO}_2\text{Na}\cdot 2\text{H}_2\text{O}$ 298
 - N*-benzoylacrylamides 416
 - N*-benzyl-substituted 1-imino-2,2,2-trifluoroethyl-
 - phosphonates 785
 - N*-bromosuccinimide (NBS) 198, 322, 741
 - n*- Bu_4NI 76, 311, 455
 - N*- CH_2CF_3 motif
 - electrophilic trifluoroethyl
 - sources 753–756
 - trifluoroethylamine 752–753
 - N*- CF_2H azaheterocycles 730
 - N*- CF_2H pyridinones 732
 - N*- CF_2H motif
 - by decarboxylative
 - reactions 728–733
 - difluoromethyldiarylsulfoniums 733
 - chlorodifluoromethyl phenyl
 - sulfone 733
 - from halodifluoromethanes 726
 - nucleophilic
 - difluoromethylation 737

- TMSCF₂Br 737
 TMSCF₂Cl 737
 TMSCF₃ 737
N-tosyl-*S*-difluoromethyl-*S*-phenylsulfoximine 736
N-CF₃ amines 747
N-CF₃ benzimidazoles 747
N-CF₃ imidazole and pyrazole 747
N-CF₃ motif
 electrophilic
 trifluoromethylation 743
 fluorination by bromine
 trifluoride 742
 fluorine/halogen exchange 739
 nucleophilic
 trifluoromethylation 750
 oxidative desulfurization–fluorination of
 dithiocarbamates 741–742
 oxidative desulfurization–fluorination of dithiocarbamoyl disulfides 739–740
 radical trifluoromethylation 743
 via thiocarbamoyl fluoride 743
N-CF₃ triazoles 750, 751
N-chloro-*N*-(phenylsulfonyl) benzenesulfonamide 330
N-(cyanosulfanyl)-aniline 778
N-difluoromethylation 728, 731–735, 737, 739
N-difluoromethyl(benz)imidazolin-2-ones 159
N-(diphenylmethylidene) 184
N-difluoromethyl-2-pyridones 728, 730
N-difluoromethyl thioureas 732
 Negishi aryl–aryl bond-forming cross coupling reactions 660
N-fluorobenzenesulfonimide (NFSI) 272, 329, 628
N-fluorosulfurylation 633, 634
N-(*gem*-difluorocyclopropyl) azoles 180
N-(hetero)aryl-*N*-hydroxylamines 202, 230
N-heterocyclic carbene (NHC) 6, 218, 513, 647, 737
 NH sulfoximines 680, 681, 683, 685, 686, 688
 Ni-catalyzed
 trifluoromethylthiolation 349
 nickel-catalyzed cross-coupling
 bromodifluoroacetamides 37
 difluoroalkyl bromides 36
 nickel-catalyzed difluoroalkylation
 difluoroalkylated sulfones 42
 unactivated difluoroalkyl
 bromides 41
 nickel-catalyzed difluoromethylation
 arylboronic acids,
 bromodifluoromethane 15
 (DMPU)₂Zn(CF₂H)₂ 10
 iododifluoromethane 18
 nickel-catalyzed reductive
 difluoromethylation
 aryl chlorides, bromides 16
 1-nitro-3-and 4-(pentafluorosulfanyl) benzenes 554
 1-nitro-3-(pentafluorosulfanyl) benzenes 553
 1-nitro-4-(pentafluorosulfanyl) benzene 555
 4-nitrophenyl(phenyl)(trifluoromethyl) sulfonium salt 302
 nitroso arenes 743, 750
N-methylmorpholine (NMM) 512
N-methyl-*N*-CF₃-aminopyridine 741
N-methyl-*N*,3-
 diarylpropiolamides 395
N-methyl-*N*-phenyl-*S*-(trifluoromethyl) thiohydroxylamine 385, 387, 389–390
N-methyl-*N*-phenyl-
 trifluoromethanesulfenamide
 II 325
N,N-diethylaminosulfur trifluoride (DAST) 47
N,N'-dimethylpropyleneurea (DMPU) 172
N,N-dimethyl-*S*-difluoromethyl-*S*-phenylsulfoximinium
 tetrafluoroborate salt 736
N,N,N',N'-tetramethyl-ethane-1,2-diamine (TMEDA) 19

- N*-OCF₃ reagents
N-trifluoromethoxy
 benzimidazole 211
N-trifluoromethoxy triazolium
 salts 215
n-perfluorobutane sulfonyl fluoride
 (PBSF) 655
N-phenyl-2,2,2-trifluoroacetamide 755
N-phenyl-trifluoromethanesulfenamide
 I 325
N-protected 4-
 (phosphonodifluoromethyl)-
 L-phenylalanines 788
 [N-(*p*-toluenesulfonyl)imino]
 phenyliodinane 682
N-(pyridin-2-yl)-acetamide 728
N-(2-pyridyl)indoles 359
N-SCF₃ phthalimide 422
N-*t*-butanesulfinyl
 glycosylamines 774
N-*t*-butyl- α -phenylnitron (PBN) 246
N-(*tert*-butanesulfinyl)imines 120
N-*tert*-butylsulfinyl ketimines 120
N-Tf S-R_F sulfilimine 677
N(TMS)₃/Me₄NF 295
N-tosyl-*S*-difluoromethyl-*S*-
 phenylsulfoximine 496, 736
N-trifluoromethanesulfenamides 419
N-trifluoromethoxy
 benzimidazole 211
N-trifluoromethoxy pyridine salts 242
N-trifluoromethoxysaccharin 213
N-trifluoromethoxy triazolium
 salts 214, 216
N-trifluoromethyl-*N*-
 nitrosobenzenesulfonamide
 (CF₃N(NO)SO₂Ph) 301
N-trifluoromethyl-*N*-
 nitrosotrifluoromethane-
 sulfonamide (CF₃N(NO)
 SO₂CF₃) 301
N-(trifluoromethyl)
 phthalimide 387
N-trifluoromethylthioaniline 389, 432
N-(trifluoromethylthio)-
 bis(phenylsulfonyl)
 imide 329–330
N-trifluoromethylthio-
 dibenzenesulfonimide 344,
 383–384
N-trifluoromethylthiodibenzene-
 sulfonimide
 (PhSO₂)₂NSCF₃ 425
N-trifluoromethylthio-4-
 nitrophthalimide 421
N-(trifluoromethylthio)
 phthalimide 321, 323, 353, 419,
 437
N-trifluoromethylthiosaccharin 320,
 328, 344, 383, 387, 423
N-trifluoromethylthiosuccinimide 322,
 345, 419, 423
N-trimethylsilyl-
 bis(trifluoromethanesulfonyl)
 imide (TMSNTf₂) 245
 nucleophilic difluoroalkylation
 BrCF₂CO₂Et and BrCF₂CH=CH₂ 89
 silanes 94
 XCF₂PO(OEt)₂ 90
 XCF₂SO₂Ar 90–93
 nucleophilic difluoromethylation 737
 cadmium, copper and zinc
 reagents 90
 miscellaneous reagents 96
 PhSO₂CF₂Br 92
 PhSO₂CF₂CO₂K 93
 PhSO₂CF₂H 90–92
 PhSO(NTBS)CF₂H 96
 reagents 94
 sulfoximine reagent 96
 TMSCF₂H 94
 nucleophilic fluorination 274, 279,
 739, 770
 pre-existing ring system 138,
 140–142
 nucleophilic monofluoromethylation
 CH₂FI 124
 2-fluoro-1,3-benzodithiole-1,1,3,3-
 tetraoxide 123
 fluorobis(phenylsulfonyl)
 methane 121–122
 fluoromalonates 119
 fluoromethyl phenyl
 sulfone 119–120

- 2-fluoro-2-sulfonylketone 122
- monofluoromethyl phosphonium salts 124
- PhSO(NTBS)CH₂F 123–124
- TMSCF(SO₂Ph)₂ (TFBSM) 123
- nucleophilic trifluoromethoxylation
 - alkyl alcohols 259–260
 - alkyl electrophiles 258
- nucleophilic trifluoromethylation 295
 - CF₃Se moiety 694
 - N-CF₃ motif 750
- nucleophilic trifluoromethylthiolating reagent 381
- nucleophilic
 - trifluoromethylthiolation 378
 - cesium trifluoromethylthiolate 434
 - copper trifluoromethylthiolate 437–439
 - reaction with bis(trifluoromethylthio) mercury Hg(SCF₃)₂ 434
 - reaction with other nucleophilic SCF₃ reagents 439–443
 - silver trifluoromethylthiolate 435–437
- nucleophilic trifluoromethylthiolation reagents
 - 2,2'-bipyridine copper trifluoromethylthiolate ((bpy) CuSCF₃) 313–314
 - bis-(trifluoromethylthio) mercury [Hg(SCF₃)₂] 309–310
 - cesium trifluoromethylthiolates (CsSCF₃) 315
 - copper trifluoromethylthiolate (CuSCF₃) 312–313
 - silver trifluoromethylthiolate (AgSCF₃) 311–312
 - tetramethylammonium (Me₄NSCF₃) 315–316
- O**
- O-benzoyl oximes 410
- OCFHCH₃ group 267, 285
- OCF₂H group
 - decarboxylative fluorination 272
 - difluorocarbene into O–H bond 269–272
 - difluoromethoxylation 273–274
 - direct electrophilic
 - difluoromethylation 272–273
 - fluorination 278–280
 - monofluoromethylation 275–278
 - nucleophilic fluorination 274
- OCF₃ motif
 - decarboxylative
 - fluorination 199–200
 - direct
 - trifluoromethylation 200–202
 - fluoroformates 198
 - indirect construction of 198
 - intramolecular OCF₃ migration 202–203
 - oxidative fluorodesulfurization 198
 - trifluoromethyl ethers 197–198
- OCH₂CF₃ group
 - trifluoroethoxylation 281–283
 - trifluoroethylation 283–295
- O-octadecyl-S-
 - trifluorothiolcarbonate 442
- optically active diethyl *N*-(*p*-toluenesulfonyl)-aziridine 2-phosphonates 790
- orally available tissue-selective
 - androgen receptor modulator 752
- organofluorine fragment 654
- organometallic
 - trifluoromethoxides 217–219
- organophotocatalyst 4CzIPN and BINOL-based phosphorothiois 413
- ortho-alkynyl functionalized aryl compounds 709
- ortho-lithiation of
 - triflylarenes 509
- ortho-substituted–SCF₃ arenes 483
- O-SCF₃ reagents in direct C(sp³)–SCF₃ bond formation reactions 428
- O-tosyl α-(phenylsulfonyl)
 - difluoromethyl alcohols 526
- O-triflyl-2-(trimethylsilyl)phenols 507
- o*-(trimethylsilyl)aryl triflates 349
- oxidation of SF₅-aromatics 606

- oxidative desulfurization–fluorination
 - of dithiocarbamates 741–742
 - of dithiocarbamoyl
 - disulfides 739–740
 - oxidative difluoromethylation
 - phenanthridines 22
 - 1,10-phenanthrolines 22
 - oxidative fluorodesulfurization
 - method 198
 - oxidative radical intermolecular
 - phosphonotri
 - fluoromethylthiolation 409
 - oxidative radical intermolecular
 - trifluoromethylthioarylation of
 - styrenes 406
 - oxindole compounds 415
 - oxindole-derived alkenes 381
 - oxodifluoroalkylation,
 - $\text{BrCF}_2\text{CO}_2\text{Et}$ 105
 - oxytrifluoromethylthiolation
 - of α -diazoketones 427
 - of alkylsilanes 411
 - ozone depletion chemical 300
 - ozone depletion potential (ODP) 728
- p**
- palladium-catalyzed cross-coupling
 - α,α -difluoroketones 38
 - bromides with difluoroenol
 - silyl 37
 - bromodifluoroacetamides 31
 - bromodifluoroacetate 31
 - palladium-catalyzed decarbonylative
 - difluoromethylation,
 - $(\text{DMPU})_2\text{Zn}(\text{CF}_2\text{H})_2$ 7
 - palladium-catalyzed difluoroacetylation,
 - aryl bromides/triflates 31
 - palladium-catalyzed
 - difluoromethylation
 - arylboronic 19
 - aryl zinc reagents 19
 - bromodifluoroacetate via a
 - difluorocarbene pathway 8–9
 - $(\text{SIPr})\text{Ag}(\text{CF}_2\text{H})$ 6
 - TMSCF_2H 7
 - $(\text{TMEDA})\text{Zn}(\text{CF}_2\text{H})_2$ 8
 - palladium-catalyzed difunctionalization,
 - alkene 255
 - palladium-catalyzed
 - phosphonyldifluoromethylation
 - bromodifluorophosphonate 27
 - difluorophosphonyl copper
 - reagents 28
 - p*-(chlorophenyl) derivative 500
 - Pd-catalyzed asymmetric Tsuji
 - decarboxylative allylic
 - alkylation 454
 - Pd-catalyzed hydrodeoxygenation of
 - phenols 665
 - Pd(II)-catalyzed oxidative
 - trifluoromethoxylation,
 - alkenes 252–255
 - pentafluorosulfanyl (SF_5)
 - aliphatic 571–606
 - aromatics
 - elemental fluorine 554–558
 - silver difluoride (AgF_2) 552–554
 - xenon difluoride 554
 - heteroaromatics
 - arylsulfurchlorotetra
 - fluorides 558–565
 - cis*-isomer 558
 - 2-fluoro-1-(pentafluorosulfanyl)
 - benzene 569
 - iodine pentafluoride 565
 - 1-(pentafluorosulfanyl)
 - naphthalenes 569
 - 2-(pentafluorosulfanyl)pyridines 553,
 - 562
 - pentafluorosulfanyl-tetrafluoroethyl
 - derivatives
 - $(\text{SF}_5\text{CF}_2\text{CF}_2\text{X})$ 599–601
 - perfluoroalkylated sulfoximines 675,
 - 680
 - perfluoroalkyl iodides (PFAIs) 11,
 - 793
 - perfluoroalkyl phosphonic and
 - phosphinic acids 765,
 - 792–793
 - perfluoroalkylsulfurane 219
 - perfluoroalkylsulfurane
 - oxide 219–220

- perhalogenated 3-dithietanes
1, 502, 505
- pharmaceutically important
trifluoromethionine 298
- phase-transfer catalyst (PTC) 145,
202, 302, 423
- 9,10-phenanthrenequinone (PQ) 5
- phenylsulfonyl difluoroacetate salt 93
- (phenylsulfonyl)difluoromethyl boronic
acid 537–538
- phenyl-tetrazole (PT) 132
- phenylthiodifluoromethyl-
trimethylsilane
(PhSCF₂TMS) 95
- phenyl triazolinone derivatives 726
- 4-(phosphonodifluoromethyl)-L-
phenylalanine (F₂Pmp) 788
- phosphonotrifluoromethylthiolation of
unactivated alkenes 409, 410
- phosphorous-based fluoromethylating
reagents 770–785
- phosphorus-containing
reagents 103–104
- photocatalyzed
cyanodifluoromethylation of
alkenes 61–62
- photochemical radical
trifluoromethylthiolation under
UV irradiation 403–405
- photoredox catalysis (PC) 16, 49, 56,
71, 104–106, 108, 110, 128, 130,
269, 391, 413, 454, 514, 515, 675
- photoredox-mediated intramolecular
carbotrifluoromethylthiolation
reaction 416
- PI3 Kinase inhibitor 752
- Plausible reaction mechanism 79
- polar hydrophobicity 612
- polyfluoroalkoxylated (hetero)
arene 234
- polyhalogenalkyl thioethers,
fluorination of 292–293
- polysulfonates 641–643
- (poly-triflyl)alkanes 519
- potassium bis(triflyl)methide 517
- P–R_F-containing molecules
- achiral fluoro-organophosphines
766
- BrCF₂P(O)(OR)₂ 774
- chiral fluoro-organophosphines
766–770
- difluoromethylated
aminophosphonate
derivatives 787–788
- fluorophosphonium and
fluoroalkylphosphonium
cations 793–801
- HCF₂P(O)(OR)₂ 773
- monofluoroalkylated
aminophosphonate
derivatives 788–792
- monofluoromethyl
phosphonates 770–772
- perfluoroalkyl phosphonic
and phosphinic acids
792–793
- [Ph₃P⁺CF₂CO₂[−]] 779–784
- [Ph₃PCF₂X]⁺ Y[−] (X = H, Cl, Br,
I; Y = Cl, Br, I, OTf)
779–784
- TMSCF₂P(O)(OR)₂ 777–779
- trifluoromethylated
aminophosphonate
derivatives 785–787
- trifluoromethylphosphonate
reagents 784–785
- propionic acids 392, 393, 397, 408
- protein tyrosine phosphate
(PTPase) 23
- P*-stereogenic ferrocene-derived
(trifluoromethyl)
phosphanes 768
- p*-toluenesulfonyl azide
(TsN₃) 750
- pyrazole triflones 513
- pyrazolin-5-ones 368
- pyridine-methyl-
dithiocarbamate 741
- pyridine-oxazoline (Pyox)
ligand 254
- pyridinium chlorochromate
(PCC) 70, 586

pyridinyl- and thionyl-based
fluorosulfates 631
pyridin-2-yl fluorosulfates 631

q

quaternary α -chloro- α -
trifluoromethylthiolated
aldehydes 423

r

radical 3, 11, 16–23, 31, 39, 47, 56, 59,
69, 73, 75, 76, 101–112, 128, 147,
184, 185, 208, 214, 231, 233, 234,
238–248, 251, 260, 272, 298–302,
391–398, 498, 577–580
radical C–H bond
difluoromethylation 19–22
radical difluoromethylation
heteroarenes with
ArI(OCOCF₂H)₂ 21
heteroarenes with HCF₂COOH 22
heteroarenes with
Zn(SO₂CF₂H)₂ 21
radical monofluoromethylation 128–130
radical photocatalytic
oxytrifluoromethylthiolation of
styrenes 416
radical trifluoromethylation 743
CF₃Se moiety 693–713
radical trifluoromethyl-
selenolation 712–713
radical trifluoromethylthiolation
with the aid of anionic SCF₃
reagents 405–411
methods 391
processes 396
radical trifluoromethoxylation,
alkenes 251–252
Ramachary–Bressy–Wang enamine
[3+2] cycloaddition 751
(*R*)-2,2'-binaphthol 766
reagents for
trifluoromethylthiolation 369
regioselective *o,o'*-(bis)
trifluoromethylthiolated
products 345
reticulated vitreous carbon (RVC) 64

Rh-catalyzed
trifluoromethylthiolation 359
ring-closing
trifluoromethylthiolation 411
R₃N⁺CF₂H ammoniums 736
Ru(bpy)₃Cl₂/TEA 298
Ru(bpy)₃Cl₂/TMEDA 298
Ruppert–Prakash reagent 145,
169–182, 187, 202, 364, 376, 381,
419, 477, 478, 579, 640, 641, 679,
694, 697, 701, 706, 737, 743, 749,
750

s

S-alkyl *S*-phenyl tosylsulfoximines 680
Sandmeyer-type trifluoromethylthiolation
reaction 348
S-aryl sulfoximines 681
S-(bromodifluoromethyl)
diarylsulfonium salts 97
SCF₂CO₂Et-containing electron rich
(hetero)arenes and ketones 471
SCF₂CO₂Et cysteine analog 469
SCF₃-containing compounds 291
SCF₃-containing spirocyclopentanone–
thiochromanes 322
SCF₂H moiety, direct formation of
C–SCF₂H bond 453–462
SCF₂PO(OEt)₂-containing alkynes 466
SCF₃-substituted alkenes and alkynes
electrophilic trifluoromethylthiolation
381–391
via manipulation of SCF₃-containing
building blocks 374–376
nucleophilic trifluoromethylthiolation
377–381
radical trifluoromethylthiolation
methods 391–398
via *S*-trifluoromethylation 376–377
SCF₃-substituted allenes via
nucleophilic
trifluoromethylation 376
SCF₃-substituted pyrrolidines and
piperidines 428
Schotten–Baumann reaction 590
Schwesinger's superbase (*t*-BuP₄)
496

- S*-(difluoromethyl)
 benzenesulfonylthioate 460
S-(difluoromethyl)diarylsulfonium
 tetrafluoroborate reagent 733
 SF₅-acetylene 602–605
 SF₅CF₂CF₂Br
 α,β-unsaturated ketones 601
 cycloalkadienes 601
 SF₄CF₃ derivatives
 aliphatic and olefinic 614
 ¹³C NMR chemical shifts 613
 inductive effect 612
S-(fluoromethyl)
 benzenesulfonylthioate 463
 Shen–Lu reagent 319–321, 428
 Shen reagent 328–329
 Shen's trifluoromethylsulfonate
 reagent 431
 Shibata's reagent 331, 333, 334
 Shibata's trifluoromethylsulfonyl
 hypervalent iodonium ylide
 reagent 382, 383, 387
 Sildenafil 282, 743
 silicon-mediated aldol condensations, of
 octyl SF₅-acetate with electron-
 rich benzaldehydes 596
 silicon-mediated Mukaiyama aldol
 reactions, of octyl SF₅-acetate
 with aldehydes 596
 silver(I)-catalyzed
 trifluoromethoxylation of
 alkenes 255
 silver difluoride (AgF₂)
 arylsulfur pentafluorides 554
 diphenyl disulfide 552
 1-nitro-3,5-bis(pentafluorosulfanyl)
 benzene 552, 553
 1-nitro-3-(pentafluorosulfanyl)
 benzenes 553
 nitro-substituted diphenyl
 disulfides 552
 2-(pentafluorosulfanyl)pyridine 553
 silver(I) trifluoromethylthiolate
 (AgSCF₃) 311, 406, 433, 435
 single electron transfer (SET) 11, 147,
 213, 231, 239, 269, 383, 391, 397,
 411, 512, 527, 696, 728
 (SIPr)Ag(SCF₂H) 453
S-(monofluoromethyl)diarylsulfonium
 tetrafluoroborate 125–126
 (1*S*)-(–)-*N*-trifluoromethylthio-2,10-
 camphorsultam 331, 428
 sodium
 2-(4-bromophenyl)-1,1-
 difluoroethanesulfinate 49
 sodium chlorodifluoroacetate
 (SCDA) 150, 187, 728, 730
 sodium perfluoroalkanesulfonates
 (R_FSO₂Na) 360
 sodium sulfonates 320
 sodium triflate 413, 487, 488, 508,
 510, 695, 696, 743
 sodium trifluoromethanesulfonate
 (CF₃SO₂Na) 334
 sodium trifluoromethylsulfinate 507,
 510, 695
 Sonogashira reactions 660, 661
S-((phenylsulfonyl)difluoromethyl)
 thiophenium salts 100–101
S–R_F sulfoximines
 fluorination of *S*-alkyl
 sulfoximines 679–680
 by imination of sulfoxides 680–682
 isolation of *S*–R_F sulfilimines
 and 686–688
 by oxidation of
 sulfilimines 682–683
 post functionalization 688
 Stille coupling with vinyl tin
 reagents 660
S-(trifluoromethyl)
 benzenesulfonylthioate
 (PhSO₂SCF₃) 415
 structure-activity relationship
 (SAR) 248
 3-substituted silyl aryl triflates 349
 substituted *N*-CF₃ triazoles 751
 sulfenamide *N*-SCF₃ reagent 346
 sulfentrazone 726, 728
 (phosphadifluoromethyl)sulfinyl
 indoles 504
 sulfonamides 643, 646
 sulfonylimidazolium bifluoride
 product 646, 647

- sulfonyl oxygen–LA interactions 622
- sulfuramidimoyl fluorides 669
- sulfur-fluoride exchange (SuFEx) 622, 623, 636, 638, 639, 641–643, 646–650, 665–669
- aryl sulfonyl fluorides 623
- fluorosulfates 665
- N*-acyltyrosine 622
- nucleophilic addition/elimination mechanism 621–622
- p*-NO₂ phenyl sulfonyl fluoride 622
- polysulfonates 642–643
- sulfonamides 643–647
- sulfones 638–641
- sulfonic esters 641–643
- sulfur (VI) fluorides
 - cross-coupling reactions, SO₂F group 649–654
 - fluorine and sulfur sources 626–630
 - fluorosulfates 630–636, 656–668
 - naked method 624
 - organofluorine chemistry 654–656
 - potassium bifluoride approach 624
 - properties and reactivity of 621–623
 - in situ* sulfonyl chloride formation 625–626
 - sulfamoyl fluorides 630–636
 - sulfuramidimoyl fluorides 669
 - tandem organic reactions 647
- sulfur hexafluoride (SF₆) 571, 611
- t**
- telcagepant 752
- temperature-sensitive
 - trifluoromethoxylating reagent 229
- terbinafine 743
- terminal alkynes 97, 320, 381, 387–390, 394, 455, 461, 480, 510, 663, 701, 711, 778, 782
- tetraalkyl fluoromethylene
 - bisphosphonates [(RO)₂P(O)]₂CHF 772
- tetrabutylammonium fluoride (TBAF) 296, 302, 536, 626, 655, 679, 771
- tetrabutylammonium
 - triphenyldifluorosilicate (TBAT) 171, 221, 297
- tetrakis(diethylamino)ethylene (TDAE) 500
- tetrakis(dimethylamino)ethylene (TDAE) 92, 297, 571, 695, 707
- 1,1,3,3-(tetrakis(trifluoromethane-sulfonyl)propane 519
- 1-tetralone 459
- tetramethylammonium
 - (Me₄NSCF₃) 94, 259, 315–316, 381, 441, 701–705
- tetramethylammonium
 - trifluoromethylselenolate (Me₄NSeCF₃) 701–705
- 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) 230
- 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) 62
- tetra-*n*-butylammonium bromide (TBABr) 391
- thermally stable *N*-heterocyclic carbene Ag(CF₂H) complexes 737
- thiocarbamoyl fluoride 740, 742–743
- ((2-phenylpropan-2-yl)oxy) (trifluoromethyl) thioether 320–321
- thiolates/thiols, electrophilic trifluoromethylation of 293–294
- TiCl₄-mediated aldol condensations, of ethyl SF₅-acetate 597
- TiCl₄-mediated aldol reactions, of methyl SF₅-acetate 597
- Togni reagents 202, 231, 294, 387, 749
- toltrazuril 291, 449
- toxic trifluoromethanethiol (CF₃SH) 404
- transition-metal catalyzed
 - difluoroacetylation 26–33
- transition-metal-catalyzed/mediated
 - monofluoromethylation
 - CH₂FBr 131
 - CH₂FI 130–131

- PhSO_2CHFI 131
 $\text{PTSO}_2\text{CH}_2\text{F}$ 132
 transition-metal catalyzed
 phosphonyldifluoro-
 methylation 23–26
 transition-metal catalyzed radical
 difluoromethylation 11–19
 transition-metal-catalyzed
 reactions 252
 transition-metal-free oxidative
 (phenylsulfonyl)
 difluoromethylation 526
 1,2,3-triazole based
 sulfonamides 646
 trichloroacetonitrile (Cl_3CCN) 626
 trichloroisocyanuric acid
 (TCICA) 565, 626
 2,4,6-trichloro-1,3,5-triazine (TCT
 cyanuric chloride) 754
 triethylamine 298, 591, 643, 662, 663
 triethylborane-mediated radical
 pentafluorosulfanylation
 577–580
 triflinyl heteroarenes 485, 487–489
 trifluoroacetaldehyde 297, 753, 754
 trifluoroacetate salts 295
 trifluoroalkylation 659
 2,2,2-trifluorodiazethane 755
 trifluoroethoxylation 267, 280–283, 285
 trifluoroethylamine 752–755
 2,2,2-trifluoroethylamine 752–755
 trifluoroethylation 283–284
 trifluoromethanesulfenamide
 (CF_3SNH_2) 317
 trifluoromethanesulfonyl acetate
 ($\text{CH}_3\text{CO}_2\text{SCF}_3$) 318
 trifluoromethanesulfonyl chloride
 (CF_3SOCl) 317–318, 404
 trifluoromethanesulfonyl
 trifluoroacetate
 ($\text{CF}_3\text{CO}_2\text{SCF}_3$) 318
 trifluoromethanesulfinamides 297
 trifluoromethanesulfinyl chloride
 (CF_3SOCl) 335, 336, 457, 485,
 488, 490
 trifluoromethanesulfinyl furan 487
 trifluoromethanesulfone (triflone) 675
 trifluoromethanesulfonyl chloride
 ($\text{CF}_3\text{SO}_2\text{Cl}$) 334, 432
 trifluoromethanesulfonyl diazo
 reagent 432
 trifluoromethanesulfonyl hypervalent
 iodonium ylide 353, 358, 359,
 431–432
 trifluoromethoxylated (hetero)
 arenes 227
 trifluoromethoxylated aromatics 225
 trifluoromethoxylation
 alkyl alcohols and alkyl silanes 259
 alkyl halides and alkyl triflates 258
 α -diazo esters 263–264
 C–H bonds 260–262
 of epoxides, nucleophilic 262–263
 trifluoromethyl arylsulfonate
 (TFMS) 237, 238, 255
 trifluoromethylated α - and β -
 aminophosphonates
 785–786
 trifluoromethylated aminophosphonate
 derivatives 785–787
 trifluoromethylated and
 trifluoromethylthiolated
 compounds 353
 trifluoromethylated Barton
 ester 303
 trifluoromethylating agents 215, 301
 trifluoromethylation of thiones/
 thioureas 302–303
 trifluoromethylation of thiorenes 302
 trifluoromethylation reagent 94, 200,
 202, 272, 281, 360, 419, 681, 749
 trifluoromethylazosulfonylarenes
 ($\text{CF}_3\text{N}_2\text{SO}_2\text{Ar}$) 301, 505
 trifluoromethyl benzoate
 (TFBz) 222–223, 234, 236, 237
 trifluoromethyl diethylaminosulfur
 difluoride
 (CF_3 -DAST) 432–433
 trifluoromethyl ethers,
 fluorination 197–198
 trifluoromethylphosphonate
 reagents 765, 784–785
 trifluoromethylselenocyanate
 (CF_3SeCN) 708

- trifluoromethylselenoisocyanate (CF_3SeNCO) 708
 - trifluoromethylselenolated α,β -unsaturated carbonyl compounds 701
 - trifluoromethylselenolated alkynes 709
 - trifluoromethylselenolated benzofuranes 709
 - trifluoromethylselenotoluene sulfonate (CF_3SeTs) 707, 710–711
 - trifluoromethylsulfinyl (triflinyl) arenes 478
 - trifluoromethyl sulfonates (TFMS) 221
 - trifluoromethyl sulfones [RSO_2CF_3]
 - alkyl triflones 514–517
 - alkynyl 510
 - aryl triflones 505–508
 - heteroaryl triflones 513–514
 - trifluoromethyl sulfoxides [RS(O)CF_3]
 - alkyl trifluoromethyl (or perfluoroalkyl) sulfoxides 489–492
 - aryl trifluoromethyl sulfoxides 478–484
 - heteroaryl trifluoromethyl sulfoxides 484–489
 - trifluoromethylthioarenes 612
 - trifluoromethylthio lactonization/ lactamization of alkenes 425
 - trifluoromethylthiolated alkenes 330, 373–398
 - trifluoromethylthiolated alkynes 381, 387, 391, 396
 - trifluoromethylthiolated aromatics 368, 373
 - 3-trifluoromethylthiolated coumarin derivatives 394
 - trifluoromethylthiolated dithioketals 423
 - trifluoromethylthiolated functionalized heterocycles 407
 - trifluoromethylthiolated 2H-chromenes 381
 - trifluoromethylthiolated indenones 394
 - trifluoromethylthiolated oxindoles 416
 - trifluoromethylthiolated tetrahydronaphthalene skeletons 428
 - trifluoromethylthiolation/cyclization process 415
 - trifluoromethylthiolation of α -diazo esters 441
 - trifluoromethylthiolation/semi-pinacol-type rearrangement sequence 416, 419
 - trifluoromethyl trifluoromethanesulfonate (TFMT) 215–217
 - trifluoromethyltrimethylsilane (TMSCF_3) 94, 295, 737
 - 2-triflyl benzothiazole 513
 - trihalomethyl anions CF_2X^- ($\text{X} = \text{Cl}, \text{Br}$) 145
 - trimethylsilyl
 - fluorosulfonyldifluoroacetate (TFDA) 655, 732
 - difluorocarbene from 156
 - NaF system 156
 - trimethylsilyltriflate (TMSOTf) 591
 - trimethylsilyl trifluoromethanesulfonate (TMSOTf) 415
 - triphenylphosphine-mediated deoxygenative reduction process 356
 - tris(perfluoroalkyl)
 - difluorophosphoranes 793
 - tris(pentafluorophenyl)-phosphine 766
 - tris(dimethylamino)sulfonium
 - difluorotrimethylsilicate (TASF) 164, 296, 478, 640, 679
 - tris(dimethylamino)sulfonium trifluoromethoxide 215, 228
 - 2,4,6-tris(2,2,2-trifluoroethoxy)-1,3,5-triazine (TTFET) 754
- u**
- Ugi's ferrocene amine 768
 - Umemoto reagents 200, 293, 294
 - Umemoto's synthesis of SF_5 arenes 615

Umemoto-type diaryl difluoromethyl
sulfonium salts 496
unactivated alkenes 105, 108, 112, 409,
412, 413, 458
unactivated internal olefins 428
unsymmetrical diaryl *S*-
(bromodifluoromethyl)
sulfonium salts 499
UV-light-initiated method 278

V

vaniliprole 291
vicinal difunctionalized
o-trifluoromethylthiolated
iodoarenes 349
Vilsmeier–Haack formylation 182
vinyl boronic acids 387
visible light-mediated process 391

visible-light promoted decarboxylative
trifluoromethylthiolation 411,
412
visible-light promoted hydrogen atom
transfer HAT-catalyzed
trifluoromethylthiolation
413

W

weak base NaOAc mediated
reaction 348
Wittig olefination approach 376
Wurtz reaction 138

X

XCF₂SO₂Ar 90–93

Z

zinc difluoromethylsulfinate 49

