Journal of Fluorine Chemistry 133 (2012) 1–8

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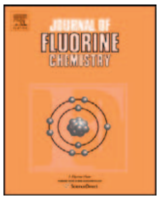

Graphical Abstracts/J. Fluorine Chem. 133 (2012) 1–8

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Preface

Qing-Yun Chen

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

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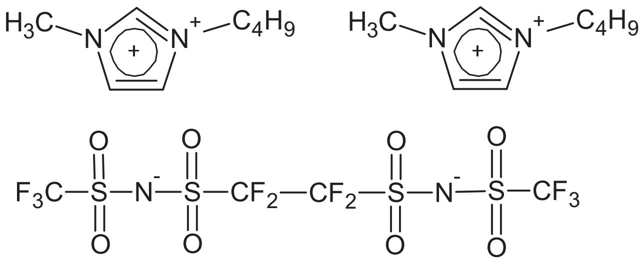
J. Fluorine Chem., 133 (2012) 11

Synthesis of 1,3-dialkyl imidazolium ionic liquids containing difunctional and tetrafunctional perfluoroalkylsulfonyl imide anions

Tom Hickman, Darryl D. DesMarteau

Department of Chemistry, Clemson University, Clemson, SC 29634-1905, USA

Direct synthesis of a difunctional RTIL.



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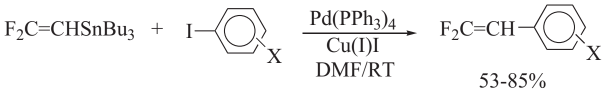
An improved, efficient route to 2,2-difluoroethenylbenzenes

Long Lu, Donald J. Burton

Department of Chemistry, The University of Iowa, Iowa City, IA 52242, USA



Treatment of vinylidene fluoride with tert-BuLi at −115 °C gave a solution of [F_2C-CHLi]. Addition of Bu_3SnCl to this lithium reagent at −110 °C gave an 88% isolated yield of F_2C-$CHSnBu_3$. Reaction of F_2C-$CHSnBu_3$ with substituted aryl iodides under Stille-Liebeskind conditions [$Pd(PPh_3)_4$/Cu(I)I] at room temperature afforded the 2,2-difluoroethenylbenzines in good yield. In the absence of the Cu(I)I co-catalyst, no reaction occurred. This work provides the most efficient route for the conversion of aryl halides to 2,2-difluorostyrenes.

doi:10.1016/S0022-1139(11)00407-6

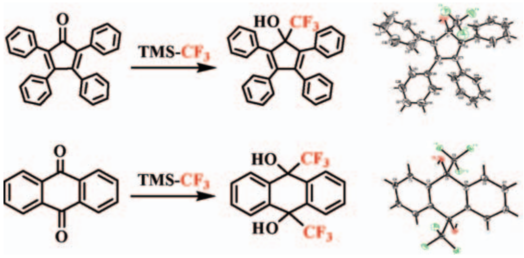
J. Fluorine Chem., 133 (2012) 20

Synthesis and characterization of novel trifluoromethyl-containing alcohols with Ruppert's reagent

Rajendra P. Singh, Jean'ne M. Shreeve

Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

Utilization of Ruppert's reagent (TMS-CF_3) enhances the formation of some novel trifluoromethylated alcohol derivatives from their corresponding ketone and aldehyde precursors.



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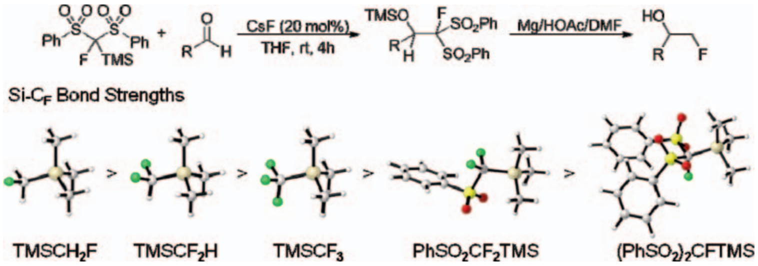
Facile synthesis of α-monofluoromethyl alcohols: Nucleophilic monofluoromethylation of aldehydes using TMSCF(SO_2Ph)$_2$

G.K. Surya Prakash, Nan Shao, Zhe Zhang, Chuanfa Ni, Fang Wang, Ralf Haiges, George A. Olah

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA, 90089-1661, USA



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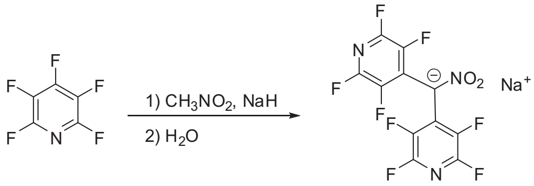
Synthesis and molecular structure of a perfluorinated pyridyl carbanion

Neil Colgin, Natalie J. Tatum, Ehmke Pohl, Steven L. Cobb, Graham Sandford

Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK

The first perfluorinated pyridyl carbanion, sodium nitrobis(perfluoropyridin-4-yl)methanide, to be characterised by X-ray crystallography is reported.



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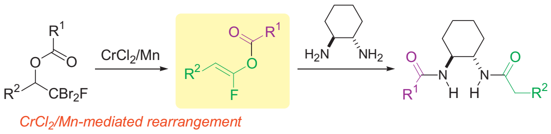
Preparation of (*Z*)-1-fluoro-1-alkenyl carboxylates, carbonates and carbamates through chromium mediated transformation of dibromofluoromethylcarbinyl esters and the reactivity as double acyl group donors



Akio Saito[a], Manabu Tojo[a], Hikaru Yanai[a], Fukiko Wada[a], Muga Nakagawa[a], Midori Okada[b], Azusa Sato[b], Rieko Okatani[b], Takeo Taguchi[a]

[a]*School of Pharmacy, Tokyo University of Pharmacy and Life Sciences, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan*
[b]*Tokyo Women's Medical University, 8-1 Kawada-cho, Shinjuku-ku, Tokyo 162-8666, Japan*

$CrCl_2$/Mn-mediated transformation of various dibromofluoromethylcarbinyl esters provided 1-fluoro-1-alkenyl esters in good yield with an excellent *Z* selective manner. 1-Fluoro-1-alkenyl ester thus obtained acts as a double acyl donor in the reaction with necleophiles such as amine, thiol, alcohol as well as bifunctional necleophiles such as ethylene diamine derivative.

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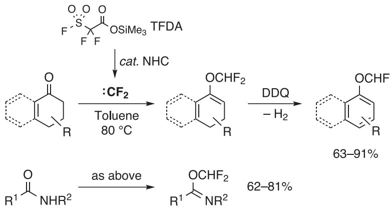
NHC-catalyzed generation of difluorocarbene and its application to difluoromethylation of oxygen nucleophiles

Kohei Fuchibe, Yuta Koseki, Tatsuya Aono, Hisashi Sasagawa, Junji Ichikawa

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571, Japan



Controlled generation of difluorocarbene was effected by NHC-catalyst under mild conditions starting from TFDA. Cyclohexenones and tetralones were difluoromethylated with the generated difluorocarbene to afford enol difluoromethyl ethers. The ethers were then dehydrogenated with DDQ to furnish aryl difluoromethyl ethers in high yield. Secondary amides also underwent difluoromethylation selectively on the oxygen atom to give difluoromethyl imidates, which allows the formation of 2-difluoromethoxypyridines.

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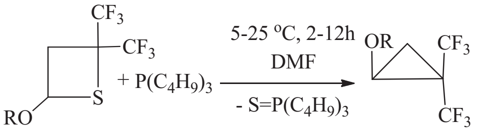
Simple synthesis of 1,1-bis(trifluoromethyl)cyclopropanes

Viacheslav A. Petrov[a], Will Marshall[b]

[a]*DuPont Central Research and Development[1], Experimental Station, PO Box 80500, Wilmington, DE 19880-0500, United States*
[b]*DuPont Corporate Center for Analytical Sciences, Experimental Station, PO Box 80500, Wilmington, DE 19880-0500, United States*



1a	**R=C_2H_5**	**2a**, 86 %
1b	**R=*n*-C_3H_7**	**2b**, 71%
1c	**R=*i*-C_3H_7**	**2c**, 75-81%
1d	**R=*n*-C_4H_9**	**2d**, 90%
1e	**R=*t*-C_4H_9**	**2e**, 70%
1f	**R=*c*-C_6H_{11}**	**2f**, 65%
1g	**R=$ClCH_2CH_2$**	**2g**, 89%

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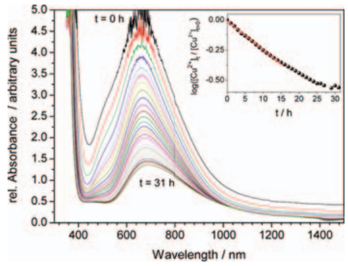
Me_3SiCF_3/AgF/Cu—A new reagents combination for selective trifluoromethylation of various organic halides by trifluoromethylcopper, $CuCF_3$

Mikhail M. Kremlev[a], Aleksej I. Mushta[a], Wieland Tyrra[b], Yurii L. Yagupolskii[a], Dieter Naumann[b], Angela Möller[c]

[a]*Institute of Organic Chemistry, National Academy of Sciences of the Ukraine, Murmanskaya St. 5, UA-02094 Kyiv, Ukraine*
[b]*Department für Chemie, Institut für Anorganische Chemie, Universität zu Köln, Greinstr. 6, D-50939 Köln, Germany*
[c]*Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA*



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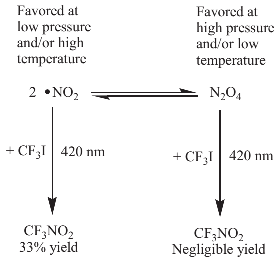
Optimization of the photochemical generation of trifluoronitromethane, CF_3NO_2, and a refined purification technique

John O. Hauptfleisch, Matthew D. Hennek, Alfred Waterfeld, Richard E. Fernandez, Joseph S. Thrasher

Department of Chemistry, The University of Alabama, 250 Hackberry Lane, Tuscaloosa, AL 35487, USA



The gas-phase photochemical generation of CF_3NO_2 from CF_3I and NO_2 was found to be equilibrium limited. The best reaction conditions allowed the generation of only 1–3 g of CF_3NO_2 per batch reaction in an approximate 16-L vessel.

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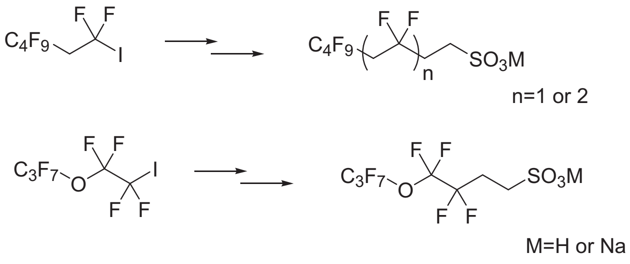
Fluorinated sulfonate surfactants

Sheng Peng[a], Ming-Hong Hung[b]

[a]*DuPont Chemical & Fluoroproducts, E.I. DuPont de Nemours & Co., Experimental Station E402/4317B, P.O. Box 80402, Wilmington, DE 19880-0402, USA*
[b]*DuPont Performance Polymer, E.I. DuPont de Nemours & Co., Experimental Station E293/202, P.O. Box 80293, Wilmington, DE 19880-0293, USA*

Synthesis of polyfluorinated sulfonate surfactants containing vinyldene fluoride (VDF, $-CH_2CF_2-$) units or ether (–O–) groups.



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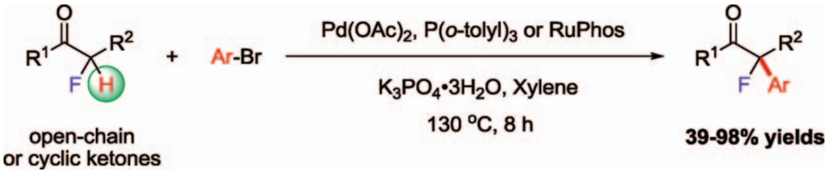
Palladium-catalyzed direct α-arylation of α-fluoroketones: A straightforward route to α-fluoro-α-arylketones



Chen Guo[a], Ruo-Wen Wang[a], Yong Guo[a], Feng-Ling Qing[ab]

[a]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China*
[b]*College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China*

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Three-component reactions involving quinoline or isoquinoline, dialkyl acetylenedicarboxylate and β-trifluoroacetyl vinyl ethyl ether

Yong Xin, Jingwei Zhao, Shizheng Zhu

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

The three-component reactions (TCRs) involving quinoline or isoquinoline, dialkyl acetylenedicarboxylate and β-trifluoroacetyl vinyl ethyl ether were investigated. The reaction proceeded smoothly under ambient temperature in DMSO to give the 4-trifluoroacetyl substituted benzo[c]quinolizine derivatives in moderate yields. However, under the same reaction condition, isoquinoline afforded the 2-trifluoromethyl substituted 1-oxa-(11H)-benzo[a]dihydroquinolizine or 4-trifluoroacetyl substituted benzo[a]dihydroquinolizine products. The possible reaction pathways were proposed.

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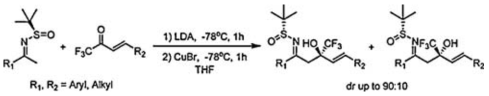
Regiospecific and diastereoselective aldol reaction of chiral *N*-sulfinyl metalloenamines with α,β-unsaturated trifluoromethyl ketones: Asymmetric synthesis of tertiary trifluoromethyl allylic carbinols

Zhen-Jiang Liu[ab], Fan Zhang[b], Jin-Tao Liu[b]

[a]*School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, China*
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*



Regiospecific and diastereoselective aldol type reaction of chiral *N*-sulfinyl metalloenamines with α,β-unsaturated trifluoromethyl ketones was reported, which affords the corresponding tertiary trifluoromethyl allylic carbinols in high yields with good diastereoselectivities (dr up to 90:10).

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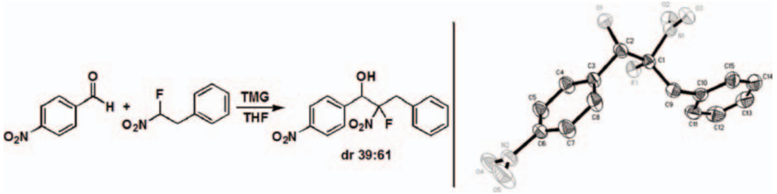
Henry reaction of fluorinated nitro compounds

Huawei Hu[a], Yangen Huang[a], Yong Guo[b]

[a]*College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Road, Shanghai 201620, China*
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China*



Henry reaction of α-fluoro nitro compounds with various aldehydes gave fluorinated nitroalcohols in moderate to good yields.

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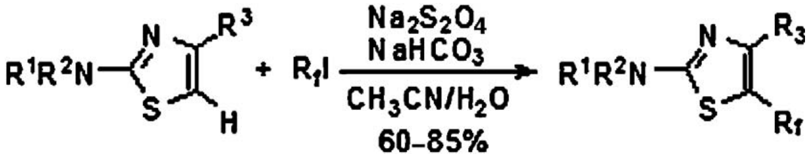
Polyfluoroalkylation of 2-aminothiazoles

Qingqing Qi, Qilong Shen, Long Lu

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China



An efficient, highly selective method for polyfluoroalkylation of 2-aminothiazole derivatives was described. Interestingly, a defluorinated reductive 2-aminothiazole derivative was obtained in moderate yields when 2-aminothiazole was reacted with $(CF_3)_2CFI$.

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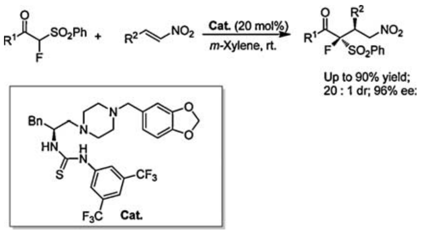
Asymmetric Michael addition of α-fluoro-α-phenylsulfonyl ketones to nitroolefins catalyzed by phenylalanine-based bifunctional thioureas

Hai-Feng Cui, Peng Li, Xiao-Wei Wang, Shi-Zheng Zhu, Gang Zhao

Key Laboratory of Synthetic Chemistry of Natural Substances and Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, China



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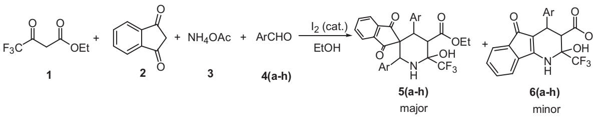
Iodine catalyzed one-pot multi-component reaction to CF_3-containing spiro[indene-2,3′-piperidine] derivatives

Baifan Dai[a], Yijun Duan[a], Xiaoqing Liu[a], Liping Song[ab], Min Zhang[a], Weiguo Cao[a], Shizheng Zhu[b], Hongmei Deng[c], Min Shao[c]

[a]*Department of Chemistry, College of Science, Shanghai University, Shanghai 200444, China*
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[c]*Instrumental Analysis and Research Center, Shanghai University, Shanghai 200444, China*



A convenient synthesis of a series of ethyl-6′-hydroxy-1,3-dioxo-2′,4′-diaryl-6′-(trifluoromethyl)-1,3-dihydrospiro[indene-2,3′-piperidine]-5′-carboxylates **5**, along with the minor product 2-trifluoromethyl-2,3,4,5-tetrahydro-1*H*-indeno [1,2-*b*]pyridine derivatives **6** from readily available starting materials via one-pot, multi-component reaction catalyzed by iodine is described.

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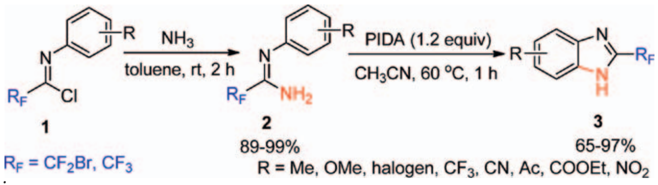
An efficient method to access 2-fluoroalkylbenzimidazoles by PIDA oxidation of amidines

Jiangtao Zhu[a], Zixian Chen[ab], Haibo Xie[a], Shan Li[a], Yongming Wu[a]

[a]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*
[b]*Department Chemistry, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China*



. A mild and practical strategy for the synthesis of 2-bromodifluoromethyl (or trifluoromethyl)-1*H*-benzimidazoles via PIDA-mediated oxidative intramolecular cyclization of the fluorinated amidines is described. The approach has the advantages of superior yields, excellent functional groups tolerance and mild reaction conditions.

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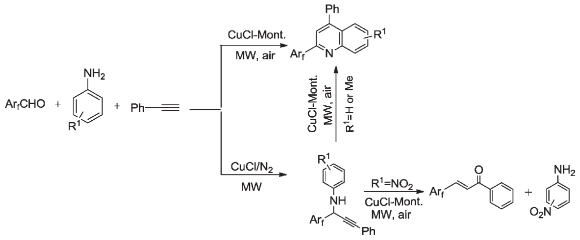
Microwave promoted one-pot preparation of fluorinated propargylamines and their chemical transformation

Xiao-Lei Chen, Jian-Min Zhang, Wen-Li Shang, Bei-Qiong Lu, Jian-An Jin

Department of Chemistry, School of Science, Shanghai University, Shanghai 200444, China



A series of fluorinated propargylamines have been synthesized from the one-pot three-component reaction of fluorobenzaldehyde, aniline and phenylacetylene under solvent-free and microwave irradiation. The fluorinated propargylamines were then further transformed to chalcones or quinoline derivatives respectively depending on the different structures of propargylamines.

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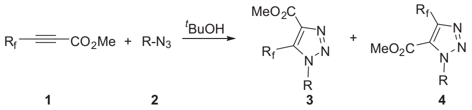
Scope and regioselectivity of the 1,3-dipolar cycloaddition of azides with methyl 2-perfluoroalkynoates for an easy, metal-free route to perfluoroalkylated 1,2,3-triazoles

Jiamei Wei[a], Jie Chen[a], Jiechao Xu[a], Long Cao[a], Hongmei Deng[d], Weihua Sheng[e], Hui Zhang[a], Weiguo Cao[abc]

[a]*Department of Chemistry, Shanghai University, Shanghai 200444, China*
[b]*State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[c]*Key Laboratory of Organofluorine Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[d]*Laboratory for Microstructures, Shanghai University, Shanghai 200444, China*
[e]*Shanghai Institute of Space Propulsion, Shanghai 200233, China*



1,3-Dipolar cycloadditions of methyl 2-perfluoroalkynoates with various azides have been examined, leading to a simple metal-free synthetic protocol for the synthesis of perfluoroalkylated 1,2,3-triazoles. The regiochemical results demonstrated that the cycloaddition was controlled by FMO (the frontier molecular obitals) interaction and steric hindrance in transition states.

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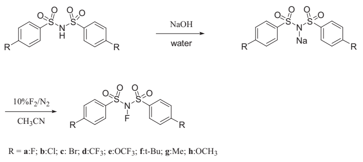
The investigation of fluorination reaction of *p*-substituted benzenesulfonimides with fluorine–nitrogen mixed gas to synthesize NFSI analogues

Guanlong Chen[a], Fuli Chen[a], Yan Zhang[a], Xueyan Yang[a], Xiaoming Yuan[a], Fanhong Wu[ab], Xianjin Yang[abc]

[a]*Key Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China*
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[c]*Wengfu Group Co. Ltd., Guizhou 550000, China*



The fluorination of the sodium salts of *p*-substituted benzenesulfonimide with 10% F_2–N_2 mixed gas in acetonitrile at room temperature could afford the corresponding N-fluoro-benzenesulfonimide (NFSI) analogues in moderate to good yields.

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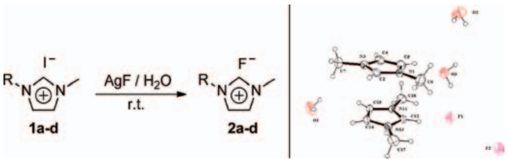
Efficient synthesis of 1-alkyl-3-methylimidazolium fluorides and possibility of the existence of hydrogen bonding between fluoride anion and C(sp^3)–H



Zhi-Qiang Zhu[a], Ming-Yue Jiang[b], Chang-Ge Zheng[b], Ji-Chang Xiao[a]

[a]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*

[b]*School of Chemical and Material Engineering, Southern Yantze University, Wuxi 214122, China*

1-Alkyl-3-methylimidazolium fluorides were successfully synthesized by the reaction of silver fluoride with the corresponding imidazolium iodides. Weak interaction between fluoride anion and C(sp^3)–H was observed as determined by single crystal X-ray diffraction analysis.

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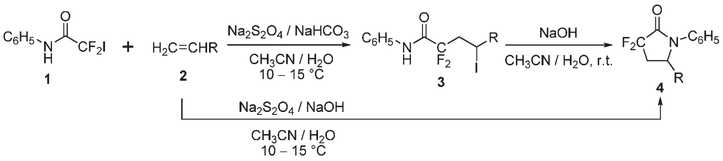
Rational and practical synthesis of α,α-difluoro-γ-lactams



Bin-Hui Li[a], Ke-Lai Li[ab], Qing-Yun Chen[a]

[a]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*

[b]*College of Chemistry and Chemical Engineering, Hunan University (HNU), Changsha 410082, China*

Treatment of *N*-phenyl-iododifluoroacetamide (**1**) with terminal alkenes (**2**) in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in CH_3CN/H_2O gave good yields of *N*-phenyl-2,2-difluoro-4-iodoalkanamide (**3**), which cyclized under strong basic conditions to afford *N*-phenyl-α,α-difluoro-γ-lactams (**4**). Or simply, these lactams **4** can be directly prepared in one-pot from **1** and **2** in the presence of $Na_2S_2O_4$ and NaOH.

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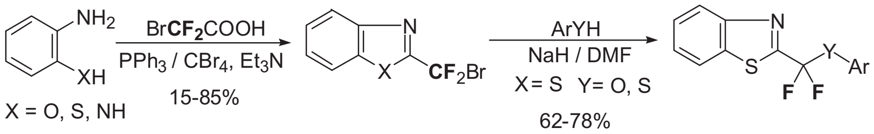
A facile preparation of 2-bromodifluoromethyl benzo-1,3-diazoles and its application in the synthesis of *gem*-difluoromethylene linked aryl ether compounds

Haizhen Jiang[a], Shijie Yuan[a], Yeshan Cai[a], Wen Wan[a], Shizheng Zhu[b], Jian Hao[ab]

[a]*Department of Chemistry, Shanghai University, Shanghai 200444, China*

[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*



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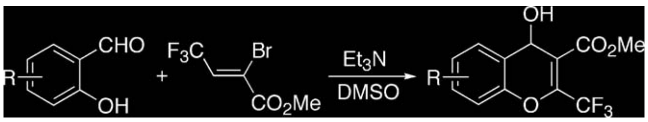
A facile synthetic route to 2-trifluoromethyl-substituted polyfunctionalized chromenes and chromones



Lele Wen, Honghai Zhang, Hao Lin, Qilong Shen, Long Lu

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

Reaction of salicylaldehydes with a novel building block-methyl (Z)-2-bromo-4,4,4-trifluoro-2-butenoate **1** in the presence of excess Et_3N under mild conditions gave methyl 4-hydroxy-2-(trifluoromethyl)-4*H*-chromenes-3-carboxylate derivatives **3a**–**j** in high yields. Treatment of **3a**–**j** with Sarrett reagent in CH_2Cl_2 gave methyl 4-oxo-2-(trifluoromethyl)-chromene-3-carboxylate derivatives **4a**–**h** with moderate to good yields.

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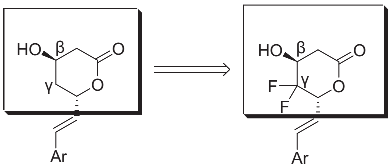
Synthesis of γ,γ-difluoro-β-hydroxy-δ-lactones as new precursors of HMG-CoA reductase inhibitor



Xiaoguang Wang[a], Xiang Fang[a], Hongyuan Xiao[a], Yan Yin[b], Huimin Xia[a], Fanhong Wu[ab]

[a]*Key Laboratory for Advanced Material and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*
[b]*School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 120 Caobao Road, Shanghai 200235, China*

A series of γ,γ-difluoro-β-hydroxy-δ-lactones **1** was efficiently synthesized as new precursors of HMG-CoA reductase inhibitor in one pot by treatment of readily prepared *gem*-difluoromethylenated acetonides **3** with trifluoroacetic acid. Contrarily, acetonides **3** could be transformed to the γ,γ-*gem*-difluoromethylenated α,β-unsaturated δ-lactones **2** through hydrolyzation and lactonization in refluxing toluene.

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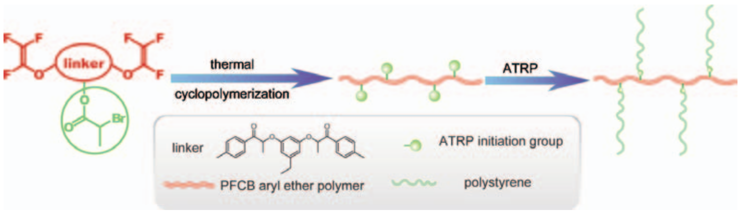
A novel semi-fluorinated graft copolymer containing perfluorocyclobutyl aryl ether-based backbone



Sen Zhang, Hao Liu, Yan Deng, Xiaoyu Huang

Key Laboratory of Organofluorine Chemistry and Laboratory of Polymer Materials, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

A series of novel semi-fluorinated graft copolymers bearing perfluorocyclobutyl (PFCB) aryl ether-based backbone and polystyrene side chains was synthesized by the combination of thermal polymerization of trifluorovinyl ether (TFVE) monomer and ATRP of styrene.