



## Graphical Abstracts/J. Fluorine Chem. 129 (2008) 889–895

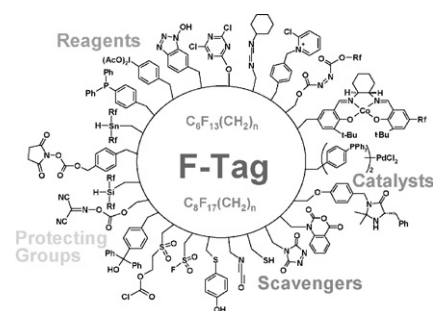
J. Fluorine Chem., 129 (2008) 898

## Fluorous chemistry in Pittsburgh: 1996–2008

Dennis P. Curran

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA

The article summarizes a lecture presented at the American Chemical Society Symposium for the 2008 Award for Creative Work in Fluorine Chemistry on 7 April 2008. A high level, historical overview of work in the fluorous field at the University of Pittsburgh is presented.



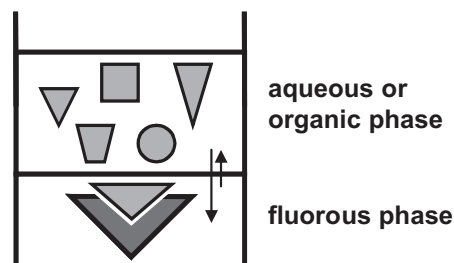
J. Fluorine Chem., 129 (2008) 903

## Noncovalent associations in fluorous fluids

Jean-Marc Vincent

Université de Bordeaux, Institut des Sciences Moléculaires, CNRS, 351 cours de la Libération, 33405 Talence Cedex, France

The confinement of receptors in perfluorocarbons, the least polar existing fluids, is emerging as a pertinent strategy to increase the strength and the selectivity of molecular recognition processes.



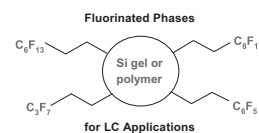
J. Fluorine Chem., 129 (2008) 910

## Fluorocarbon stationary phases for liquid chromatography applications

Wei Zhang

Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125, United States

This article presents an overview on fluorocarbon stationary phases for liquid chromatography (LC) applications. Fluorocarbons developed as alternative reverse phases have revealed previously unknown separation mechanisms and special utilities. Solvophobicity and fluorophilicity of the fluorinated phases provide enhanced selectivity for organofluorine compounds. The dual normal- and reverse-phase characteristics make fluorinated phases suitable for analysis of polar pharmaceutical and biological samples such as proteins, peptides, nucleotides, steroids, and alkaloids. Fluorinated phases for other applications, including supercritical fluid chromatography (SFC), micellar electrokinetic liquid chromatography (MEKC), ion chromatography (IC), open tubular electrochromatography (OTEC), and liquid chromatography–mass spectrometry (LC–MS) are also highlighted.

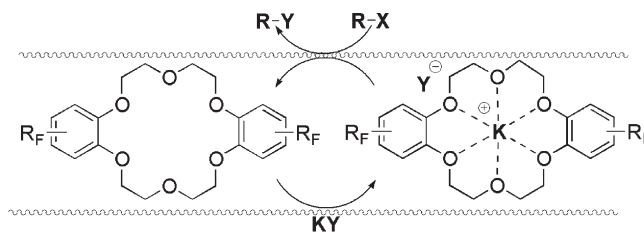


J. Fluorine Chem., 129 (2008) 920

## Fluorous phase transfer catalysts: From onium salts to crown ethers

Gianluca Pozzi<sup>a</sup>, Silvio Quici<sup>a</sup>, Richard H. Fish<sup>b</sup><sup>a</sup>CNR-Istituto di Scienze e Tecnologie Molecolari, via Golgi 19, 20133 Milano, Italy<sup>b</sup>Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, USA

Recyclable fluorous analogues of standard phase transfer catalysts are able to transfer reactive anionic species from water or from a solid surface into a second organic or perfluorocarbon phase.

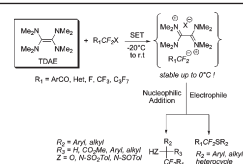


## Nucleophilic difluoromethylation and trifluoromethylation using tetrakis(dimethylamino)ethylene (TDAE) reagent

Maurice Médebielle<sup>a</sup>, William R. Dolbier Jr.<sup>b</sup><sup>a</sup>Université de Lyon, Université Claude Bernard Lyon 1 (UCBL), Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), Laboratoire de Synthèse de Biomolécules (LSB), UMR 5246 CNRS-UCBL-INSA Lyon-CPE Lyon, Bâtiment Chevreul, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France<sup>b</sup>Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA

In an effort to find new methodologies to introduce difluoromethylene and trifluoromethyl moieties into organic molecules of synthetic and biological interest, the tetrakis(dimethylamino)ethylene (TDAE) was found to be an effective reductant of a series of good electron-acceptors such as bromodifluoromethyl heterocycles, chlorodifluoromethylated ketones as well as perfluoroalkyl iodides; the corresponding anions thus generated under very mild conditions, were successfully engaged in a number of intra- and intermolecular coupling reactions with a series of electrophiles (aldehydes, ketones,  $\alpha$ -keto esters, *N*-tosyl aldimines, acyl chlorides, diol sulphates, disulfides, and diselenides). The corresponding adducts were usually obtained in moderate to good yields and the present method was found to be as good or even better as other most popular approaches. This paper gives an overview of our research efforts in this area as well as results from other groups.

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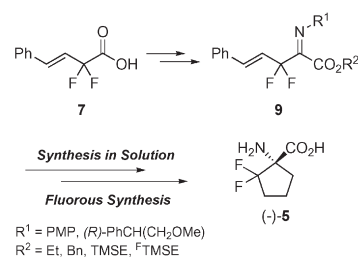


J. Fluorine Chem., 129 (2008) 943

## Solution and fluorous phase synthesis of $\beta,\beta$ -difluorinated 1-amino-1-cyclopentane carboxylic acid derivatives

Santos Fustero<sup>a,b</sup>, Vanessa Rodrigo<sup>b</sup>, María Sánchez-Roselló<sup>a</sup>, Fatemeh Mojarrad<sup>a</sup>, Ana Vicedo<sup>a</sup>, Teresa Moscardó<sup>a</sup>, Carlos del Pozo<sup>a</sup><sup>a</sup>Departamento de Química Orgánica, Universidad de Valencia, E-46100 Burjassot, Spain<sup>b</sup>Centro de Investigación Príncipe Felipe, E-46013 Valencia, Spain

An efficient protocol for the preparation of  $\beta,\beta$ -difluorinated 1-amino-1-cyclopentane carboxylic acid derivatives was developed.



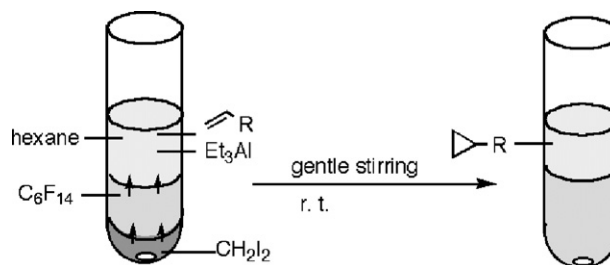
J. Fluorine Chem., 129 (2008) 951

## Cyclopropanation of alkenes with $\text{CH}_2\text{I}_2/\text{Et}_3\text{Al}$ by the phase-vanishing method based on fluorous phase screen

Hiroshi Matsubara, Masaaki Tsukida, Shinji Yasuda, Ilhyong Ryu

Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

Cyclopropanation reactions with the Maruoka-Yamamoto reagent ( $\text{Et}_3\text{Al}/\text{CH}_2\text{I}_2$ ) were carried out successfully using fluorous media as a phase screen.

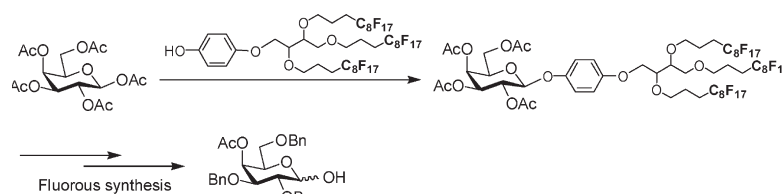


J. Fluorine Chem., 129 (2008) 955

### *p*-Alkoxyphenyl-type heavy fluorous tag for the preparation of carbohydrate units

Mamoru Mizuno, Shunsuke Kitazawa, Kohtaro Goto

Laboratory of Glyco-organic Chemistry, The Noguchi Institute, 1-8-1 Kaga, Itabashi-ku, Tokyo 173-0003, Japan



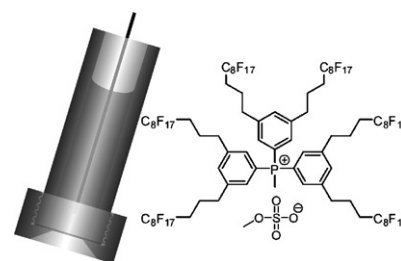
J. Fluorine Chem., 129 (2008) 961

### Preparation of a highly fluorophilic phosphonium salt and its use in a fluorous anion-exchanger membrane with high selectivity for perfluorinated acids

Paul G. Boswell, Alyce C. Anfang, Philippe Bühlmann

University of Minnesota, Department of Chemistry, 207 Pleasant St. SE Minneapolis, MN 55455, United States

The synthesis and characterization of a new fluorophilic phosphonium salt and its characterization as a cationic site in the first fluorous potentiometric anion-exchanger electrode is presented. The fluorous-membrane sensor exhibited the exceptional selectivity of  $3.9 \times 10^{10}$  to 1 for perfluorooctanesulfonate over chloride, and of  $2.5 \times 10^7$  to 1 for perfluorooctanoate over chloride.



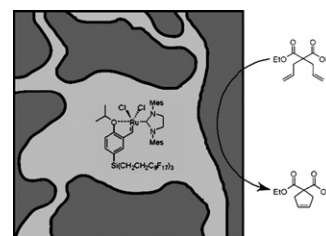
J. Fluorine Chem., 129 (2008) 968

### Ring-closing olefin metathesis in the aqueous phase of amphiphilic conetworks consisting of fluorophilic and hydrophilic compartments

Eva M. Hensle, Jan Tobis, Jörg C. Tiller, Willi Bannwarth

Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstrasse 21, D-79104 Freiburg, Germany

RCM-reactions in aqueous media using a perfluoro-tagged Hoveyda-Type catalyst, immobilized in the fluorophilic phase of amphiphilic conetworks (APNCs), were investigated.

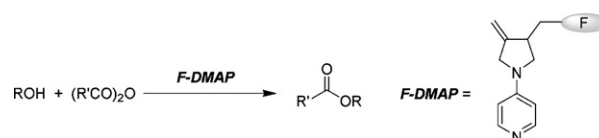


J. Fluorine Chem., 129 (2008) 974

### Fluorous analogues of DMAP (F-DMAP): Reusable organocatalysts for acylation reaction

Julien Legros, Benoît Crousse, Danièle Bonnet-Delpon

Laboratoire BioCIS-CNRS, Faculté de Pharmacie, Univ Paris-Sud, Rue J. B. Clément, F-92296 Châtenay-Malabry, France



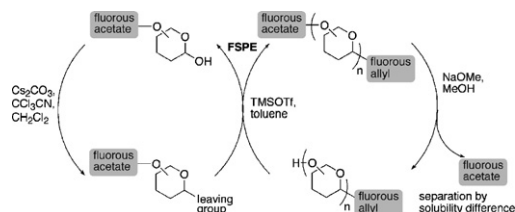
J. Fluorine Chem., 129 (2008) 978

## Mono- vs. di-fluorous-tagged glucosamines for iterative oligosaccharide synthesis

Gisun Park, Kwang-Seuk Ko, Aleksandra Zakharova, Nicola L. Pohl

Department of Chemistry and the Plant Sciences Institute, 2756 Gilman, Iowa State University, Ames, IA 50011, USA

A light fluorous acetate protecting group on an oligoglucosamine glycosyl donor allowed facile separation by FSPE of the resulting double-fluorous-tagged glycosylation product from the single-fluorous-tagged acceptor as well as donor by-products. This double-fluorous-tagging strategy offers a robust simple separation to eliminate failed glycosylation sequences in solution-based oligosaccharide synthesis.



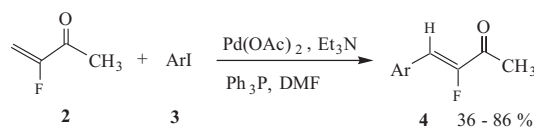
J. Fluorine Chem., 129 (2008) 983

## Heck reaction with 3-fluoro-3-buten-2-one

Timothy B. Patrick, Titus Y. Agboka, Keith Gorrell

Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026 USA

Ketone **2** reacts with aryl iodides (**3**) in a Heck reaction catalyzed by Pd(OAc)<sub>2</sub> to give Z-3-fluorobenzalacetones (**4**) in 36–86% yield.

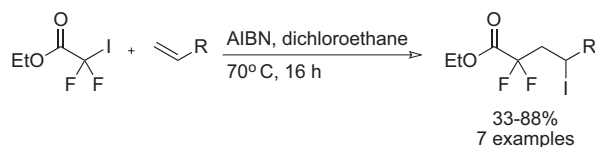


J. Fluorine Chem., 129 (2008) 986

## A convenient AIBN-initiated radical addition of ethyl iododifluoroacetate to alkenes

Leo Leung, Bruno Linclau

School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

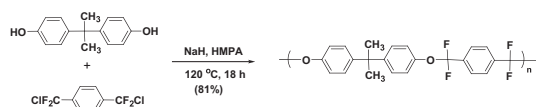


J. Fluorine Chem., 129 (2008) 991

## Novel fluoropolymers formed by an unprecedented S<sub>RN</sub>1 condensation polymerization mechanism

William R. Dolbier Jr.<sup>a</sup>, Valerie Rodriguez-Garcia<sup>a</sup>, Kai Wu<sup>a</sup>, Alexander Angerhofer<sup>a</sup>, Lotfi Hedhli<sup>b</sup>, Maher Elsheikh<sup>b</sup><sup>a</sup>Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, United States<sup>b</sup>Arkema, Inc., 900 First Avenue, King of Prussia, PA 19406-0936, United States

A condensation copolymerization reaction between bis-phenol A and *p*-bis-(chlorodifluoromethyl) benzene, likely proceeding via an unprecedented S<sub>RN</sub>1 mechanism, has produced a novel fluoropolymer.



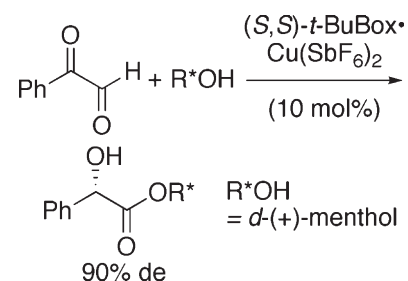
J. Fluorine Chem., 129 (2008) 994

### Asymmetric intramolecular Cannizzaro reaction of anhydrous phenylglyoxal

Kazuaki Ishihara, Takayuki Yano, Makoto Fushimi

Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

Double asymmetric induction was achieved in the reaction of anhydrous phenylglyoxal with *D*-(+)-menthol promoted by a (*S,S*)-*t*-BuBox-copper(II) hexafluoroantimonate complex.



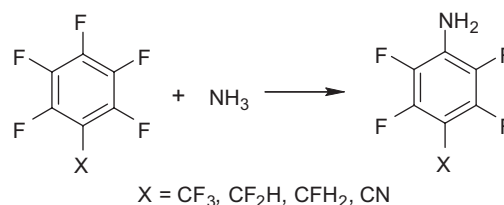
J. Fluorine Chem., 129 (2008) 998

### Mechanisms of reactions of halogenated compounds. Part 7.[1] Effects of fluorine and other groups as substituents on nucleophilic aromatic substitution

Richard D. Chambers, Peter A. Martin, Graham Sandford, D. Lyn H. Williams

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

The influence of CN, CF<sub>3</sub>, CF<sub>2</sub>H and CFH<sub>2</sub> on nucleophilic aromatic substitution reactions is established.

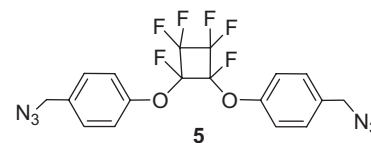


J. Fluorine Chem., 129 (2008) 1003

### Synthesis of novel aromatic ether polymers containing perfluorocyclobutyl and triazole unites via click chemistry

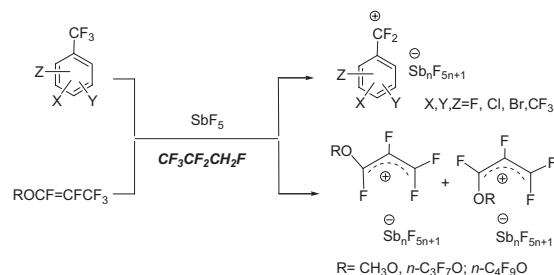
Rong-Xing Yao<sup>a,b</sup>, Lei Kong<sup>a,b</sup>, Zeng-Shen Yin<sup>a,b</sup>, Feng-Ling Qing<sup>a,c</sup><sup>a</sup>College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China<sup>b</sup>State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China<sup>c</sup>Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

A novel class of linear aromatic ether polymers containing perfluorocyclobutyl and triazole unites was prepared from the click chemistry (the copper-catalyzed Huisgen's 1,3-dipolar cycloaddition) of new monomer **5** and bisethynyl compounds.



J. Fluorine Chem., 129 (2008) 1011

### New hydrofluorocarbons (HFC) solvents for antimony pentafluoride. Generation and characterization of 1-alkoxyperfluoroallyl cations

Viacheslav A. Petrov<sup>a</sup>, Alexander Marchione<sup>b</sup>, Will Marshall<sup>b</sup><sup>a</sup>DuPont Central Research and Development<sup>1</sup>, Experimental Station, P.O. Box 0500, Wilmington, DE 19880-0500, United States<sup>b</sup>DuPont Corporate Center for Analytical Sciences, Experimental Station, P.O. Box 0500, Wilmington, DE 19880-0500, United States

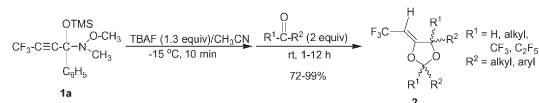
## Novel and efficient approach to (Z)-4-trifluoroethylidene-1,3-dioxolane derivatives via (trifluoromethyl)ethynylation of ketones and aldehydes

Sung Lan Jeon<sup>a</sup>, Ji Hoon Choi<sup>a</sup>, Jung Ah Cho<sup>a</sup>, Bum Tae Kim<sup>b</sup>, In Howa Jeong<sup>a</sup>

<sup>a</sup>Department of Chemistry, Yonsei University, Wonju, Republic of Korea

<sup>b</sup>Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea

Perfluoroalkylated 4-trifluoroethylidene-1,3-dioxolanes **2a–p** were prepared in quantitative yields from the reaction of new stable (trifluoromethyl)ethynylation reagent **1a** with TBAF at  $-15\text{ }^{\circ}\text{C}$  for 10 min, followed by treatment with phenyl perfluoroalkylated ketones at room temperature. The use of aldehydes under the same reaction condition afforded 1,3-dioxolanes **2q–r** in good yields. The reaction of **1a** with TBAF, followed by treatment with aldehydes or ketones at  $-15\text{ }^{\circ}\text{C}$  for 10 min and then with trifluoroacetophenone at room temperature provided 1,3-dioxolane derivatives **2s–t** in good yields. Tetrabutylammonium trifluoropropynylide [II] was treated with benzaldehyde derivatives at  $-15\text{ }^{\circ}\text{C}$  for 10 min, followed by treatment with trifluoroacetophenone, to give the corresponding 1,3-dioxolanes **2u–z** and 1,3-dioxines **3u–z** with different reaction condition.



## New aryl-containing fluorinated sulfonic acids and their ammonium salts, useful as electrolytes for fuel cells or ionic liquids

R. Arvai<sup>a,b,c,d,e,f</sup>, F. Toulgoat<sup>a,b,c,d,e,f</sup>, M. Médebielle<sup>a,b,c,d,e,f</sup>, B. Langlois<sup>a,b,c,d,e,f</sup>, F. Alloin<sup>g</sup>, C. Iojoiu<sup>g</sup>, J.Y. Sanchez<sup>g</sup>

<sup>a</sup>ICBMS, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Equipe SERCOF, 43 boulevard du 11 novembre 1918, Villeurbanne F-69622, France

<sup>b</sup>CNRS, UMR5246, Villeurbanne F-69622, France

<sup>c</sup>Université de Lyon, Lyon F-69622, France

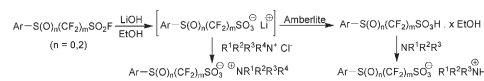
<sup>d</sup>Université Lyon 1, Lyon F-69622, France

<sup>e</sup>INSA-Lyon, Villeurbanne F-69622, France

<sup>f</sup>CPE Lyon, Villeurbanne F-69616, France

<sup>g</sup>Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, UMR 5631 CNRS-INPG-UJF, BP.75, 38402 Saint-Martin-d'Hères, France

Several aryl-containing ammonium sulfonates have been prepared either by cationic metathesis from the corresponding lithium sulfonates or from the corresponding sulfonic acids. They exhibit good conductivities and thermal properties and are promising candidates as electrolytes for electricity storage.

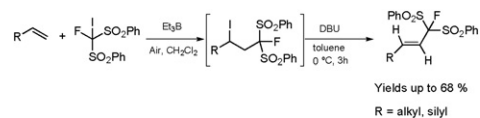


## Stereoselective synthesis of fluorobis(phenylsulfonyl)methyl-substituted alkenes using free radical fluoroalkylation

G.K. Surya Prakash, Istvan Ledneczki, Sujith Chacko, Shashank Ravi, George A. Olah

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, 837 Bloom Walk, Los Angeles, CA 90089-1661, United States

(PhSO<sub>2</sub>)<sub>2</sub>CFI was prepared in quantitative yield by the iodination of fluorobis(phenylsulfonyl)methane and utilized in facile radical bis(phenylsulfonyl)monofluoromethylation of various terminal alkenes. The synthetic methodology was further extended for the preparation of monofluoromethyl-substituted alkenes.

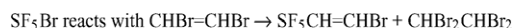


## The reaction of SF<sub>5</sub>Br with select 1,2-dihaloethylenes

Rolf Walter Winter, Gary L. Gard

Portland State University, Department of Chemistry, PO Box 751, Portland, OR 97207-0751, USA

SF<sub>5</sub>Br reacted with 1,2-dihaloethylenes in distinct ways. With X = F and Cl, the expected 1:1 addition occurred. However, when X = Br, a metathetical reaction produced the following two products in quantitative yield: SF<sub>5</sub>CH=CHBr and CHBr<sub>2</sub>CHBr<sub>2</sub>. The mechanism of this reaction is discussed.

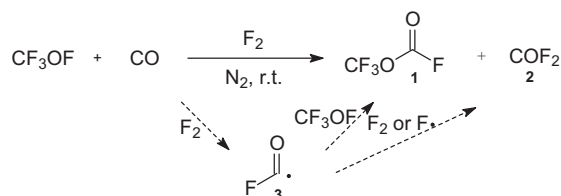


J. Fluorine Chem., 129 (2008) 1044

### A novel synthesis of trifluoromethyl fluoroformate from trifluoromethyl hypofluorite and carbon monoxide in the presence of fluorine gas

Libin Du<sup>a</sup>, Darryl D. DesMarteau<sup>b</sup><sup>a</sup>Department of Chemistry, The University of North Carolina, Chapel Hill, NC 27599, USA<sup>b</sup>Department of Chemistry, Clemson University, Clemson, SC 29634, USA

A radical reaction between CF<sub>3</sub>OF and CO initiated by F<sub>2</sub> provides a new route to the formate CF<sub>3</sub>OC(=O)F.



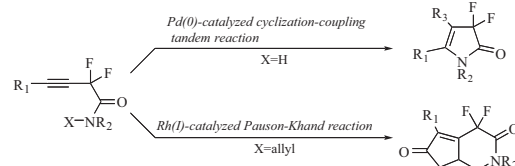
J. Fluorine Chem., 129 (2008) 1047

### Selective enhancement effects of silver salts on the transition metal-catalyzed synthesis of *gem*-difluorinated heterocyclics using 2,2-difluorohomopropargyl amides

Satoru Arimitsu, Rebecca L. Bottom, Gerald B. Hammond

Department of Chemistry, University of Louisville, Louisville, KY 40292, USA

The cationic palladium complex generated from Pd(PPh<sub>3</sub>)<sub>4</sub> (2.5 mol%) with AgSbF<sub>6</sub> (1.5 equiv.) activates the triple bond of 2,2-difluoropropargylic amides to give the 4,5-disubstituted 3,3-difluoro- $\gamma$ -lactams, through a sequential 5-*endo-dig* cyclization and cross-coupling reaction.



J. Fluorine Chem., 129 (2008) 1052

### Synthesis of trifluoromethyl alcohols from *tert*-butoxy- $\beta$ -(trifluoromethyl)styrenes and trifluoromethylbenzyl ketones under the conditions of the Leuckart–Wallach reaction

Vasiliy M. Muzalevskiy<sup>a</sup>, Valentine G. Nenajdenko<sup>a</sup>, Aleksey V. Shastin<sup>b</sup>, Elizabeth S. Balenkova<sup>a</sup>, Günter Haufe<sup>c</sup><sup>a</sup>Moscow State University, Department of Chemistry, Leninskie Gory, Moscow 119992, Russia<sup>b</sup>Institute of Problems of Chemical Physics, Chernogolovka, Moscow Region 142432, Russia<sup>c</sup>Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany