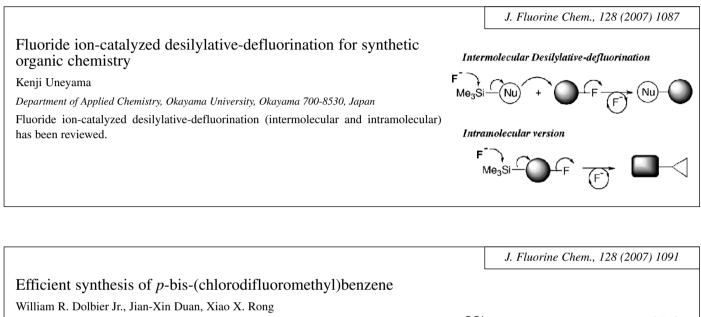


Volume 128, Issue 10, October 2007



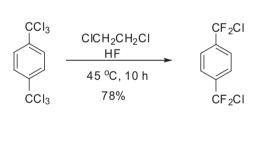
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Graphical Abstracts/J. Fluorine Chem. 128 (2007) 1075-1084



Department of Chemistry, University of Florida, PO Box 117200, Gainesville, FL 32611, United States

Selective, high yield partial fluorination of hexachloro-*p*-xylene to *p*-bis-(chlorodifluoromethyl)benzene has been accomplished by warming a slurry of the hexachloro-*p*-xylene in anhydrous HF which also contains a small quantity of inert solvent, such as 1,2-dichloroethane.

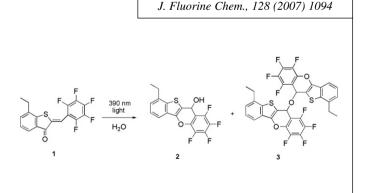


Novel photoinduced cyclization of pentafluorophenylhemithioindigo

Kiyoshi Tanaka, Kiyoshi Kohayakawa, Takayuki Irie, Satoru Iwata, Kazuto Taguchi

Laboratory of Molecular Control, Faculty of Science and Technology, Seikei University, Musashino-shi, Tokyo 180-8633, Japan

Photoirradiation of 1 causes a novel type of photoinduced cyclization, to produce the intramolecularly cyclized alcohol 2 and its dehydrated ether 3, instead of the *Z*–*E* isomerized product.

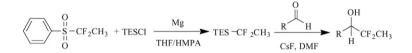


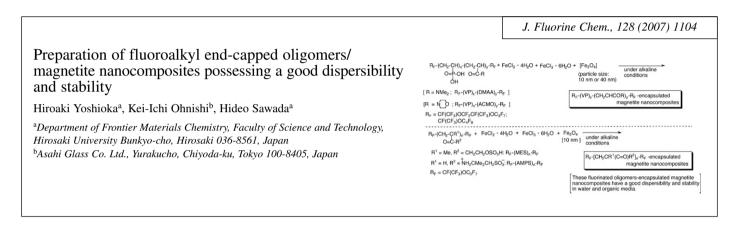
J. Fluorine Chem., 128 (2007) 1098

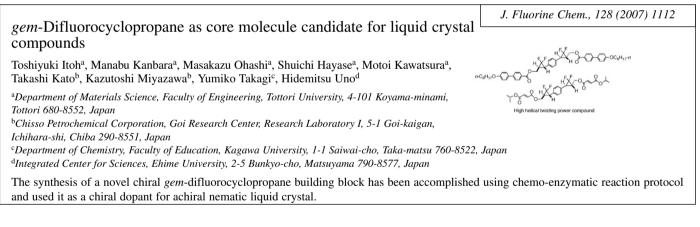
Synthesis of 1,1-difluoroethylsilanes and their application for the introduction of the 1,1-difluoroethyl group

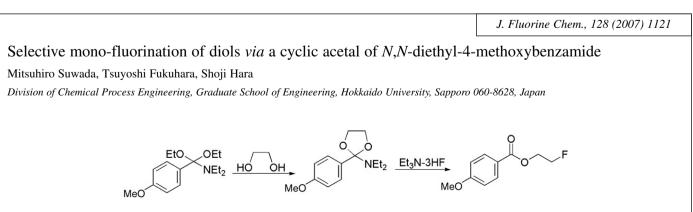
Ryo Mogi^a, Kazuo Morisaki^a, Jinbo Hu^b, G.K. Surya Prakash^c, George A. Olah^c

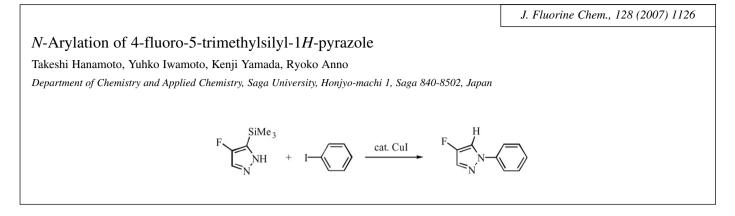
^aMizushima Research Laboratory, Kanto Denka Kogyo Co. Ltd., 4-4-8 Matsue Kurashiki, Okayama 712-8533, Japan ^bShanghai Institute of Organic Chemistry, Chinese Academy of Science, 345 Fenglin Road, Shanghai 200032, China ^cLoker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, United States

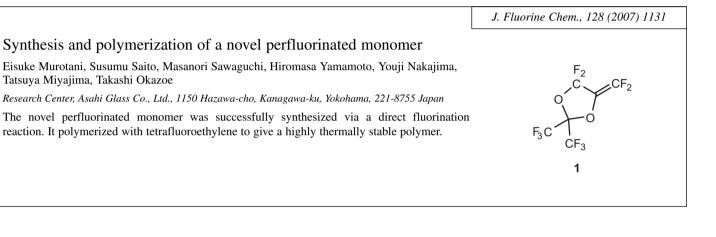


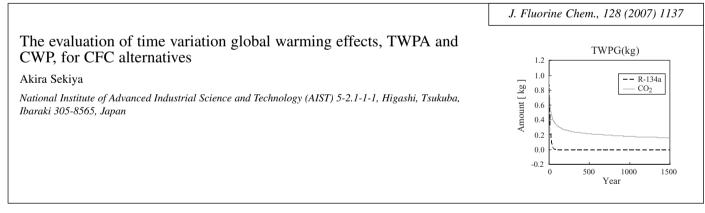












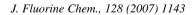
Fluorinated *N*-[2-(haloalkyl)phenyl]imidoyl chloride, a key intermediate for the synthesis of 2-fluoroalkyl substituted indole derivatives *via* Grignard cyclization process

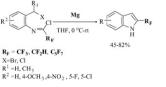
Zengxue Wang^a, Fenglian Ge^a, Wen Wan^a, Haizhen Jiang^a, Jian Hao^{a,b}

^aDepartment of Chemistry, Shanghai University, 99 Shangda Road, Shanghai 200444, China

^bKey Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China

Fluorinated N-[2-(haloalkyl)phenyl]imidoyl chloride, which was readily available from the corresponding anilines by using Uneyama's onepot synthesis of fluorinated imidoyl chloride, was found to be a key intermediate for the facile synthesis of 2-fluoroalkyl substituted indole derivatives *via* the Grignard cyclization process. The bromination of 3-methyl group of 3-methyl-2-trifluoromethyl indole with NBS/CCl₄ led to the formation of 3-bromomethyl substituted indole which can be further utilized to synthesize some new and biologically interested indole derivatives.



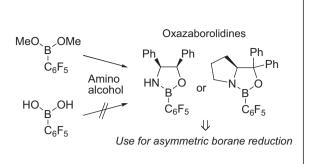


Synthesis of novel oxazaborolidines $B-C_6F_5$ and their effectiveness as asymmetric catalysts

Toshinobu Korenaga, Fuminao Kobayashi, Kenji Nomura, Shiho Nagao, Takashi Sakai

Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan

Novel oxazaborolidines B-C₆F₅ were synthesized by modified protocol from C₆F₅B(OMe)₂ in place of usual C₆F₅B(OH)₂ for investigation of the effect of C₆F₅ group in asymmetric reduction of ketones.



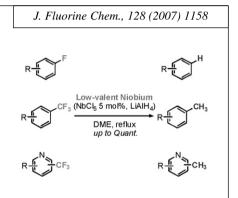
J. Fluorine Chem., 128 (2007) 1153

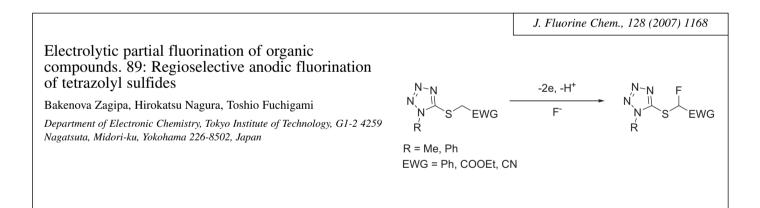
Hydrodefluorinations by low-valent niobium catalyst

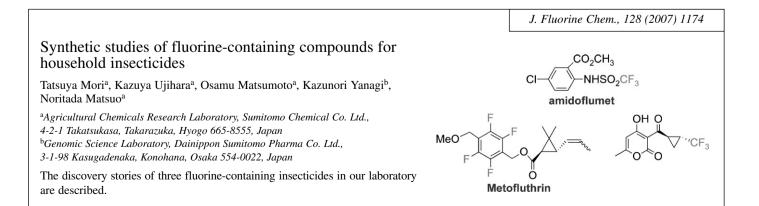
Kohei Fuchibe, Yoshitaka Ohshima, Ken Mitomi, Takahiko Akiyama

Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

Catalytic hydrodefluorinations of organofluorine compounds by low-valent niobium catalyst were developed. In the presence of niobium(V) chloride (typically, 5 mol%), fluorobenzenes, α , α , α -trifluorotoluenes and (trifluoromethyl)pyridines were hydrodefluorinated with lithium aluminum hydride to give the corresponding benzenes, toluenes and methylpyridines in good yields, respectively.







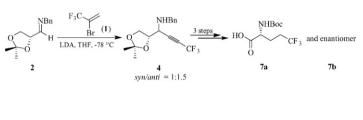
J. Fluorine Chem., 128 (2007) 1182

Nucleophilic addition of 3,3,3-trifluoropropynyllithium to D-glyceraldimine: Concise synthesis of both enantiomers of 5,5,5-trifluoronorvaline

Qi Chen^a, Xiao-Long Qiu^b, Feng-Ling Qing^{a,b}

^aKey Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Lu, Shanghai 200032, China ^bUrgitute of Biological Sciences and Biotechnology, Danchus

^bInstitute of Biological Sciences and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China



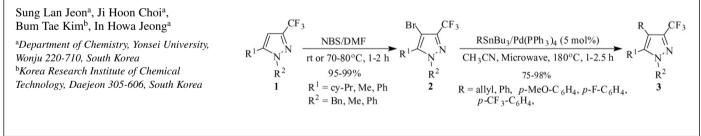
J. Fluorine Chem., 128 (2007) 1187

Practical and efficient synthesis of perfluoroalkyl iodides from perfluoroalkyl chlorides via modified sulfinatodehalogenation

Hai-Ping Cao, Qing-Yun Chen		X = F		h non an bh
Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu,	Na ₂ S ₂ O ₄		F(CF ₂ CF ₂) _n SO ₂ Na	$\xrightarrow{I_2} F(CF_2CF_2)_n I$
Shanghai 200032, China	$X(CF_2CF_2)_nCl$			
	n = 2, 3, 4	X = I, Cl	NaO ₂ S(CF ₂ CF ₂) _n SO ₂ N	Na I_2 $I(CF_2CF_2)_n I$

J. Fluorine Chem., 128 (2007) 1191

Synthesis of novel 1,4,5-trisubstituted 3-trifluoromethylpyrazoles via microwave-assisted Stille coupling reactions

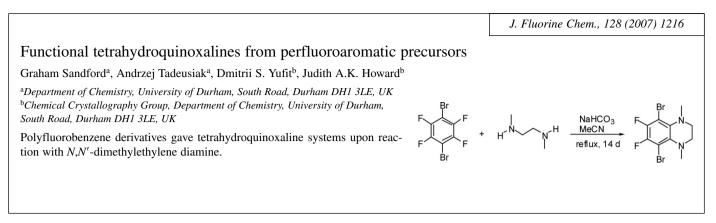


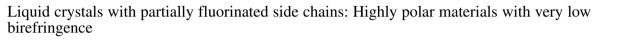
The preparation of HCF₂CdX and HCF₂ZnX *via* direct insertion into the carbon halogen bond of CF₂HY (Y = Br, I)

J. Fluorine Chem., 128 (2007) 1198 $HCF_2X \xrightarrow{M} HCF_2MX \xrightarrow{CuX} HCF_2Cu$ $X = Br, I \qquad M = Cd, Zn$

Donald J. Burton, Greg A. Hartgraves Department of Chemistry, University of Iowa, Iowa City, IA 52242, United States

Difluoromethylcadmium is readily prepared by oxidative addition of cadmium with iododifluoromethane and bromodifluoromethane. The difluoromethylcadmium reagent is thermally stable to 65–70 °C; rapid decomposition occurs at temperatures >105 °C. At room temperature the reagent is stable for weeks and only loses 31% of its activity after 2 months at RT. The difluoromethylcadmium reagent reacts readily with allylic halides at RT to give products of both α - and γ -attack in good yields. Metathesis of the difluoromethylcadmium reagent with Cu(1)X (X = Cl, Br) in DMF at -55 °C readily gives the difluoromethylcopper reagent. The copper reagent is stable only at low temperatures (-30 to -55 °C) and rapidly decomposes to HCF₂CF₂H and *cis*-CFH=CFH above these temperatures. However, HCF₂Cu is more nucleophilic than HCF₂CdX, and the copper reagent readily reacts with allylic halides at -55 °C. The regiospecificity of HCF₂Cu is vastly superior to HCF₂CdX and most of the reactions of HCF₂Cu with allylic halides occur regiospecifically. When HCF₂CdX is reacted with propargylic halides or tosylates, the predominant product is the corresponding allene. The HCF₂Cu reagent again is more reactive, completely regiospecific, and in most cases gives good isolated yields of the allenes. The HCF₂Cu reagent also readily couples with 1-iodoalkynes and 1-iodoalkynes to give good yields of the corresponding difluoromethylatyles. The HCF₂Cu reagent only undergoes alkylation with reactive alkylating agents, such as chloromethyl ethyl ether and benzyl bromide. Reaction with allylic halides, propargyl halides and 1-iodoalkynes provides HCF₂-substituted allylic halides; HCF₂-allenes and HCF₂C=R(R_p).



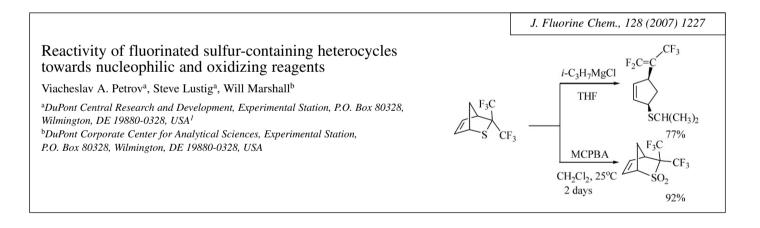


Peer Kirsch^a, Marc Lenges^b, Andreas Ruhl^b, Florian Huber^b, Richard D. Chambers^c, Graham Sandford^c

^aMerck Ltd. Japan, Liquid Crystal Technical Center, 4084 Nakatsu, Aikawa-machi, Aiko-gun, Kanagawa 243-0303, Japan

^bMerck KGaA, Liquid Crystals Division, D-64271 Darmstadt, Germany ^cUniversity of Durham, South Road, Durham, UK DH1 3LE, UK

Highly polar liquid crystals with very low birefringence were synthesized and charaterized. Their mesophases and electrooptical properties were interpreted using a detailed computational analysis of the conformational equilibrium.



J. Fluorine Chem., 128 (2007) 1235

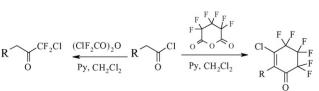
J. Fluorine Chem., 128 (2007) 1221

X, Y = H. F

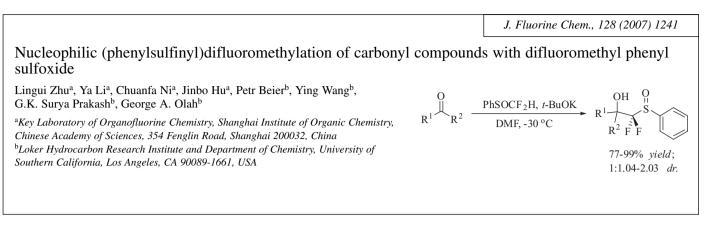
Evaluation of Zard trifluoromethylketone synthesis for the preparation of potential bifunctional fluorinated synthons

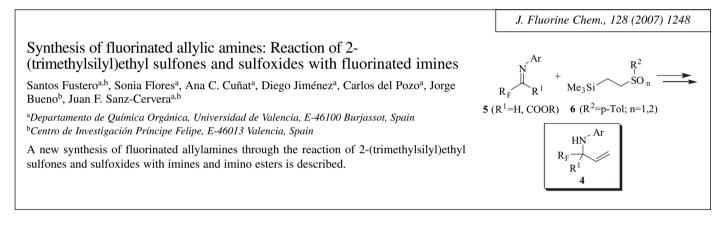
Patrick Diter, Emmanuel Magnier, Jean-Claude Blazejewski

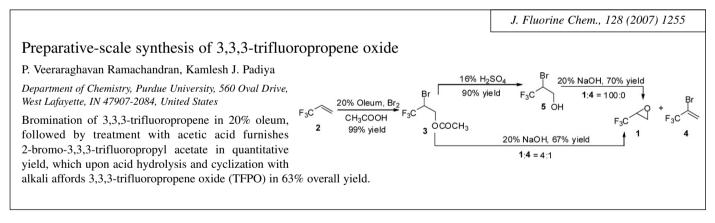
Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles, St Quentin en Yvelines, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France



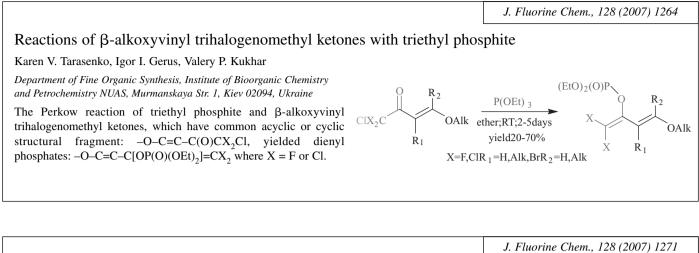
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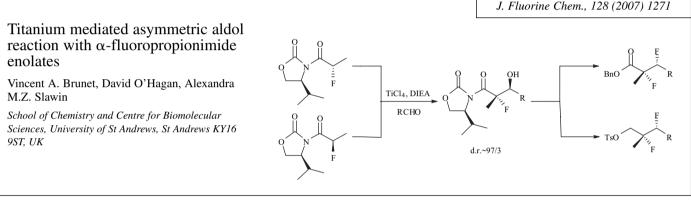






J. Fluorine Chem., 128 (2007) 1260 Simple synthesis of some unsaturated 1,1-difluoro-2-hydroxyethylphosphonates Romana Pajkert, Henryk Koroniak Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland $R_{1} \xrightarrow{P} HCF_{2}P(O)(OEt)_{2} \xrightarrow{I. f-BuL, i, THF, -90 \circ C} R_{1} \xrightarrow{R_{2}} CF_{2}P(O)(OEt)_{2}$ R1 and/or R2=H, Ph, benzylidene or cinnamylidene





J. Fluorine Chem., 128 (2007) 1280

X = OH, OR, NHR

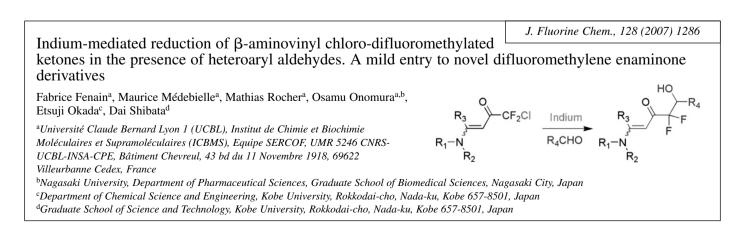
Difluoromethylene compounds as precursors to ketones, carboxylic acids, esters, amides and carbonates

Yong Guo, Jean'ne M. Shreeve

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

A review of difluoromethylene compounds as precursors to carbonyl compounds. Many ketones, carboxylic acids, esters, amides and carbonates, especially trifluoroalanine dipeptides, can be easily achieved

due to the reactivity of difluoromethylene compounds or generated through the reactive difluoromethylene intermediates.



 $\overset{\mathsf{F}}{\underset{\mathsf{R}^{1}}{\overset{\mathsf{F}}{\underset{\mathsf{R}^{2}}{\xrightarrow{}}}}} \xrightarrow{\mathsf{O}}_{\mathsf{R}^{1}} \overset{\mathsf{O}}{\underset{\mathsf{R}^{2}}{\overset{\mathsf{O}}{\underset{\mathsf{R}^{2}}{\xrightarrow{}}}}}$

1082

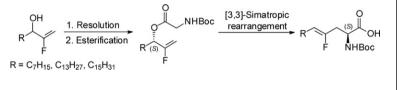
	J. Fluorine Chem., 128 (2007) 1300			
Fluoride-induced coupling of perfluoroketene dithioacetals with silyl alkynes: A way towards new polyfunctionalized trifluoromethyl building blocks				
Tiziano Nocentini, Cédric Brulé, Jean-Philippe Bouillon, Sonia Gouault-Bironneau, Charles Portella	F₃Ç SEt _{Ph} ————————————————————————————————————			
Laboratoire Réactions Sélectives et Applications, UMR 6519 CNRS, Université de Reims Champagne-Ardenne, Faculté des Sciences, BP 1039, 51687 Reims Cedex 2, France Metal free sila-Sor	$Ph \xrightarrow{CF_3} SEt \xrightarrow{TMAF (0.1 equiv.)} THF, rt \xrightarrow{CF_3} O \xrightarrow{CF_3} O \xrightarrow{CF_3} SEt \xrightarrow{TFA-H_2O 9:3} O \xrightarrow{SEt} SEt$			

J. Fluorine Chem., 128 (2007) 1306

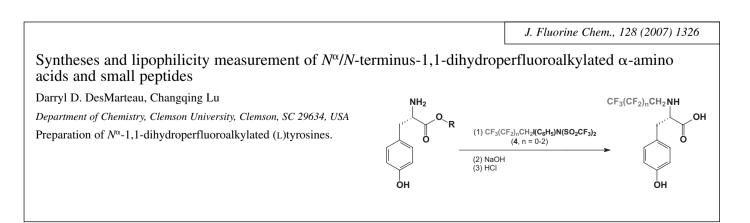
Synthesis of optically active 2-fluoroalk-1-en-3-yl esters and chirality transfer in their Claisen-type rearrangements

Michael Marhold^a, Ulrich Wittmann^a, Stefan Grimme^a, Tamiko Takahashi^b, Günter Haufe^a

^aOrganisch-Chemisches Institut, Universität Münster, Corrensstr. 40, D-48149 Münster, Germany ^bJosai International University, Faculty of Pharmaceutical Sciences, 1 Gumyo, Togane 283-8555, Japan



J. Fluorine Chem., 128 (2007) 1318 Nucleophilic trifluoromethylation of aryl halides with methyl trifluoroacetate Bernard R. Langlois^{a,b,c,d,e,f}, Nicolas Roques^{a,b,c,d,e,f} ^aICBMS, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Equipe SERCOF, 43 boulevard du 11 novembre 1918, Villeurbanne F-69622, France Cul (1 eq) Ar-CF₃ + CO₂ + MeCl $CF_3CO_2Me + Arl + CsX$ X = F, Cl DMF or Sulfolane ^bCNRS, UMR 5246, Villeurbanne, F-69622, France 45-80 % (5 eq) °Université de Lyon, Lyon F-69622, France 140-180 °C (1-2.5 eq) ^dUniversité Lyon 1, Lyon F-69622, France eINSA-Lyon, Villeurbanne F-69622, France ^fCPE Lyon, Villeurbanne F-69616, France Associated with cesium fluoride or cesium chloride and CuI, methyl trifluoroacetate (MTFA) constitutes a trifluoromethylating agent for substituting aromatic (or heteroaromatic) iodides and bromides.



J. Fluorine Chem., 128 (2007) 1335

Microfluidic behaviour of perfluoropolyether fluids in poly(dimethylsiloxane) micro-channels

Ilenia Viola^a, Giuseppe Ciccarella^a, Pierangelo Metrangolo^b, Giuseppe Resnati^b, Roberto Cingolani^a, Giuseppe Gigli^a

^aNational Nanotechnology Laboratory (NNL) of CNR, INFM, Distretto tecnologico ISUFI and Dipartimento di Ingegneria dell'Innovazione, Università degli Studi di Lecce, via Arnesano, I-73100 Lecce, Italy

^bNanostructured Fluorinated Materials Laboratory (NFMLab), Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta",

Politecnico di Milano, via Mancinelli 7, I-20131 Milano, Italy

The behaviour of different perfluoropolyether-based fluids has been studied in a microfluidic setup. It has been compared with the behaviour of a low viscosity, high-fragility polyurethane structural adhesive commonly used for the fabrication of sub-micrometer structures.

1084