

## **Perfluoroalkanesulfonic acids derivatives: synthesis and application**

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### **Abstracts**

Information of the last 10 years regarding methods of synthesis and properties of perfluoroalkanesulfonic acids and some of its derivatives is listed and analyzed here. The opportunities of using the perfluoroalkane halides and syntons on the basis of perfluoroalkylsilicon derivatives for these purposes are uncovered. The main attention is paid to practical aspects of perfluoroalkanesulfonic acids salts and bis(perfluoroalkylsulfonyl)imides using as catalysts of different processes, electrolytes, ionic liquids and N-F bond containing compounds as mild fluorinating reagents. The ways of using of perfluoroalkanesulfonic acids derivatives in organic synthesis are discussed.

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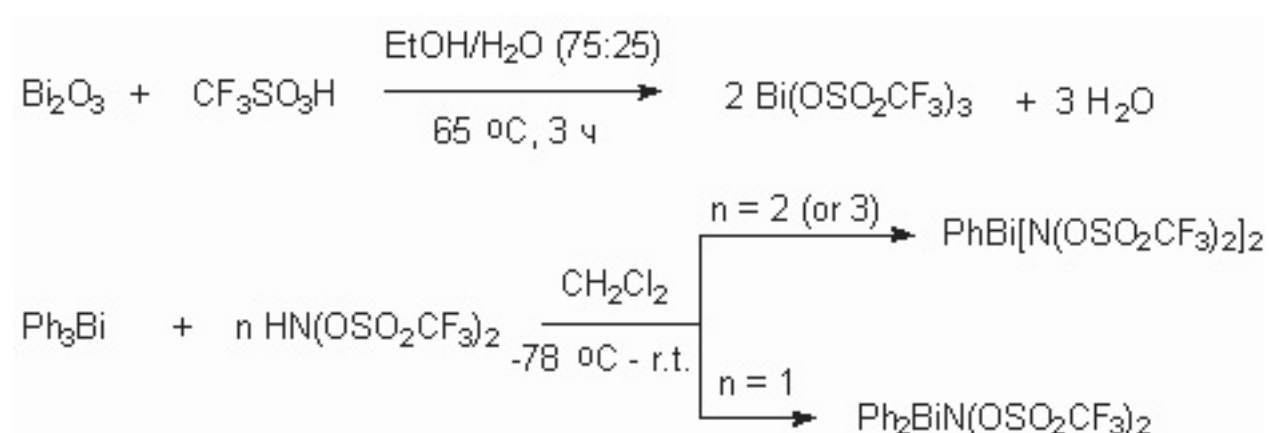
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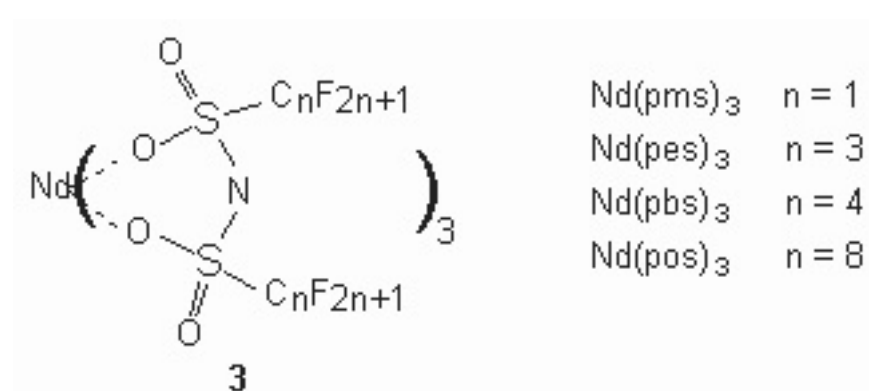
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### 3.3. Perfluoroalkanesulfo-acid salts, the catalysts of a number of chemical processes.

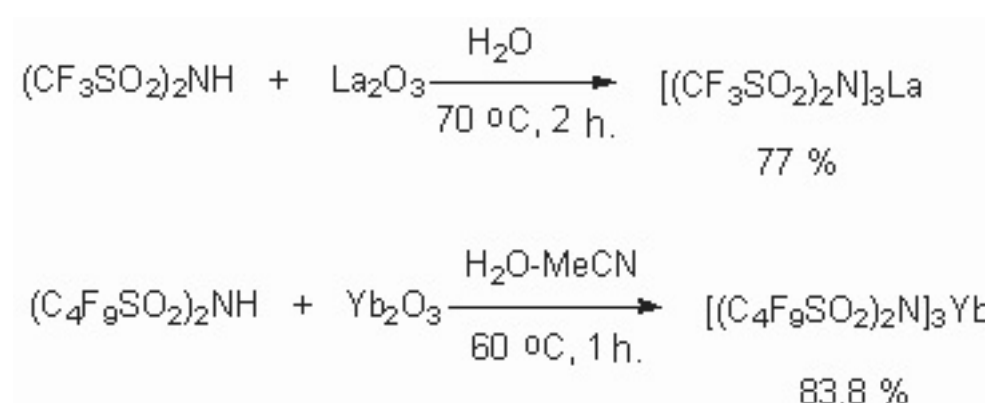
The main obtaining methods of perfluoroalkanesulfo-acids and bis(perfluoroalkanesulfonyl)imides are their interaction with corresponding oxides of elements. Thus, the reaction with bismuth oxide in the media, containing the mixture of water and ethyl alcohol [110,111] or bismuth compound [112] produces corresponding bismuth derivatives. It's better to use C1 - C3 the alcohol mixable with water, the optimal ratio water/alcohol from 1:1 up to 9:1, and molar ratio of  $\text{CF}_3\text{SO}_3\text{H}/\text{Bi}_2\text{O}_3$  is 6:1 - 6.5:1 (yield 97 %). Such salts are used as catalysts for carrying out chemical reactions of different types.



They are new ligands for lanthanide complexes creating, especially neodymium **3** [113], ytterbium and yttrium [114,115], lanthanum [116-118], europium [90] and other metals (B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Te) [119,120]. These complexes are excellent catalysts of Friedel-Crafts and in the last years there was found an application for them..  $\text{Eu}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_3$  produces luminescence with quantum yield 56.8 % [90].

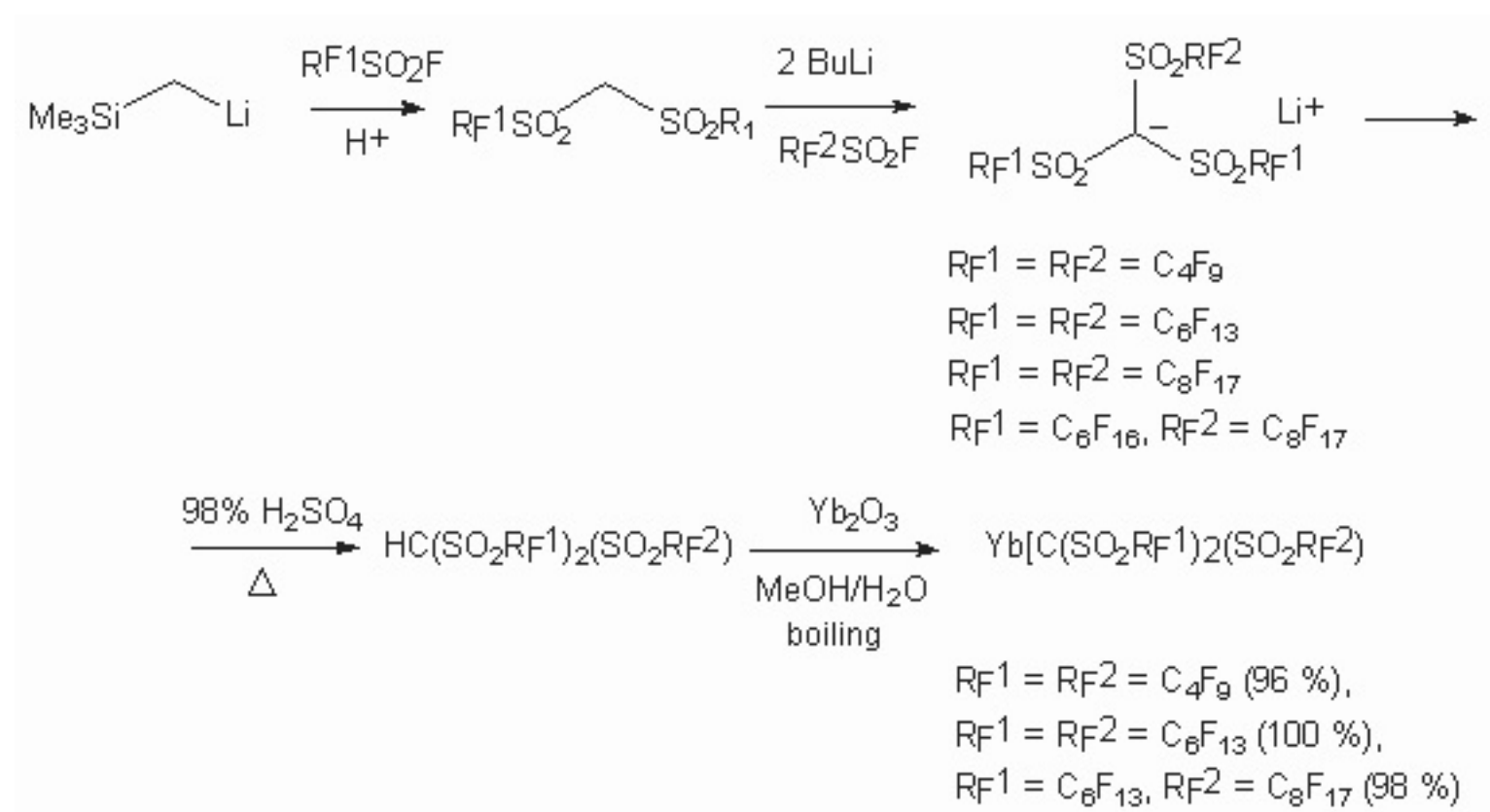


As a rule, these complexes are generated during boiling of oxides of these elements with bis(perfluoroalkanesulfonyl)imide in water for example for lanthanum:



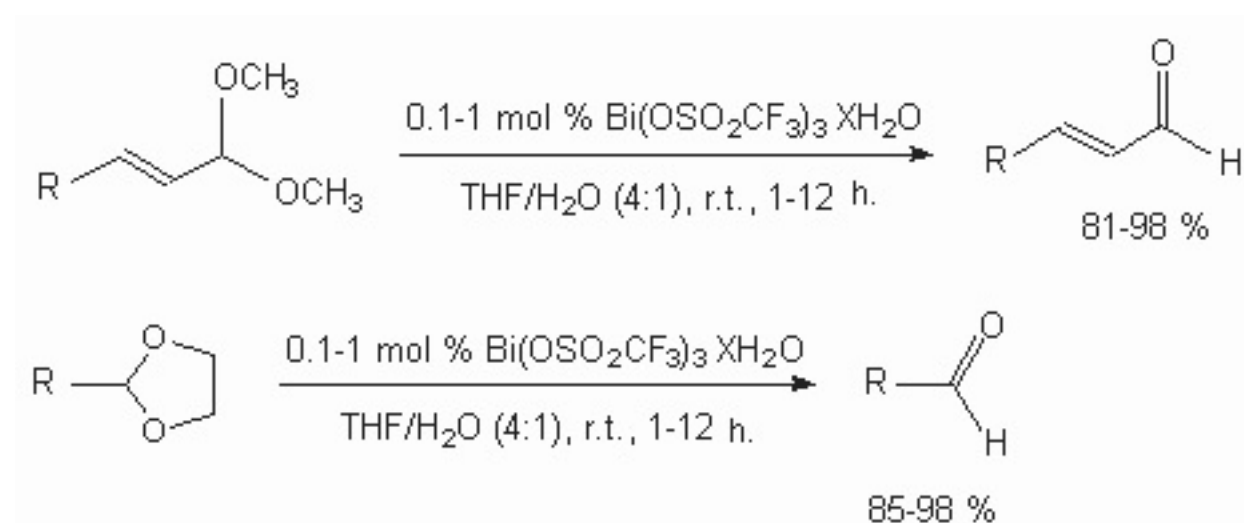
The ytterbium salts of tris(perfluoroalkanesulfonyl)**methidine** were obtained according to

the following scheme [121]:

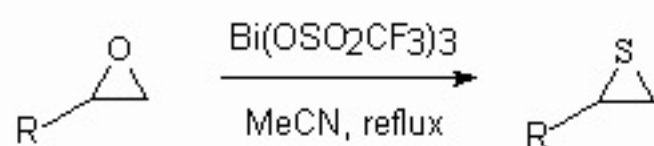


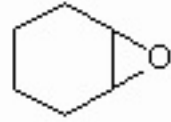
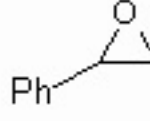


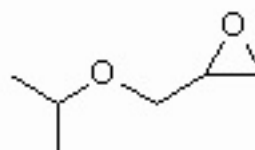
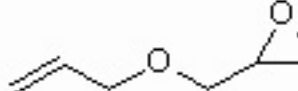

The more detailed review of data regarding application of perfluoroalkanesulfoacids is given in review [122]. We will not go beyond few new examples of their application. Thus, trifluoroalkanesulfonates of rare-earth metals are effective catalysts for example of benzyl alcohol etherification using aliphatic alcohols or thiols [123a]. In these reactions  $\text{RE}(\text{OSO}_2\text{CF}_3)_3$  can be easily returned into the process without loss of their catalytic activity.

It is shown [123b], that  $\text{Bi}(\text{OSO}_2\text{CF}_3)_3$  is an effective catalyst of acetals and ketals turning into aldehydes.

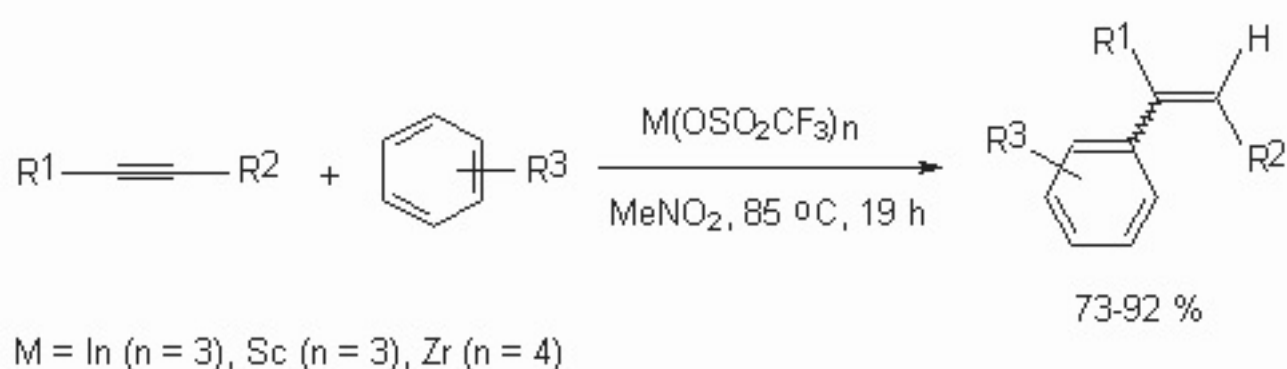


$\text{Bi}(\text{OSO}_2\text{CF}_3)_3$  catalyses epoxides turning into thiirans in the presence of ammonium thiocyanate and thiourea [123c,d].

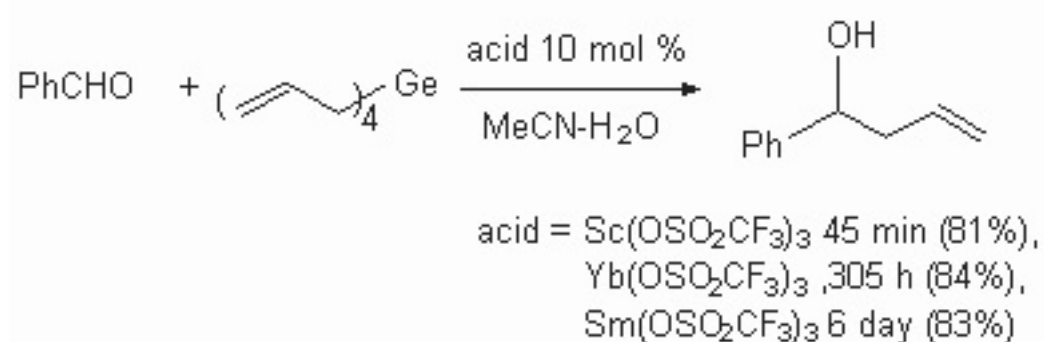


Epoxide	Bi(OSO <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> / epoxide, NH <sub>4</sub> SCN (Time, min.)	Yield, %	Bi(OSO <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> / epoxide, (NH <sub>2</sub> ) <sub>2</sub> C=S (Time, min.)	Yield, %
	0.02 (15)	99	0.05 (40)	95
	0.02 (15)	98	0.05 (60)	92
	0.02 (25)	99	0.07 (60)	90
	0.02 (10)	93	0.07 (70)	88
	0.02 (10)	97	0.07 (60)	98
	0.02 (10)	99	0.07 (90)	92
	0.02 (10)	98	0.07 (60)	93

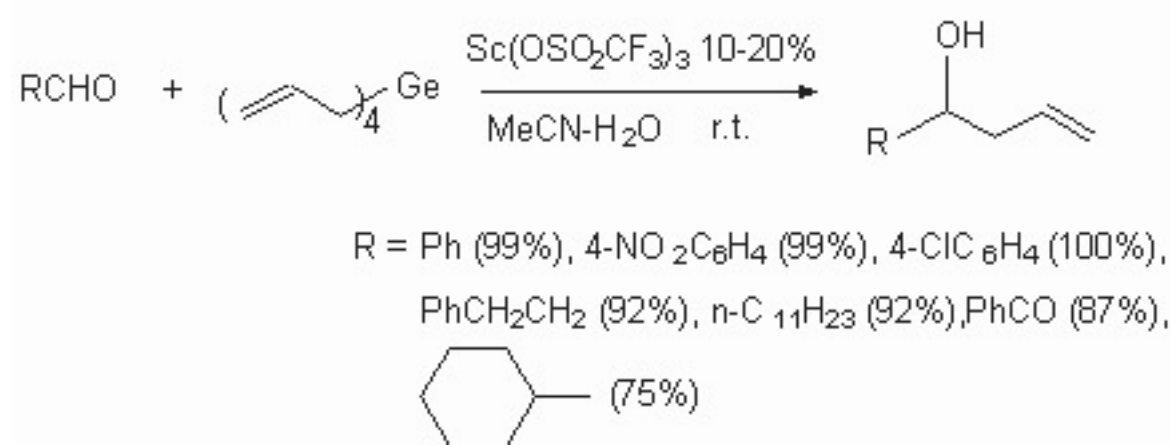
Trifluoromethanesulfonates of scandium, indium and zirconium act as effective catalysts of Friedel-Crafts alkylation of aromatic compounds by derivatives of acetylene [124].



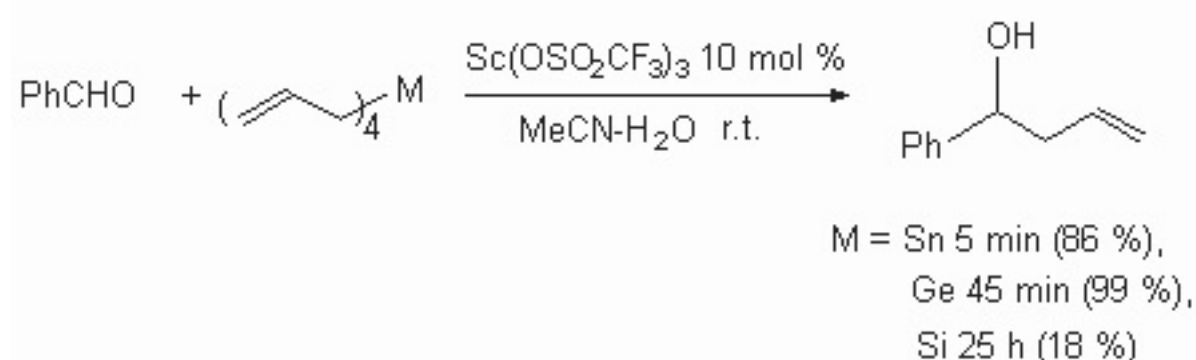
Trifluoromethanesulfonates of scandium, ytterbium and samarium appeared to be rather effective catalysts of reaction of tetrakis(allyl)germanium with carbonyl compounds, for example with benzaldehyde [125].



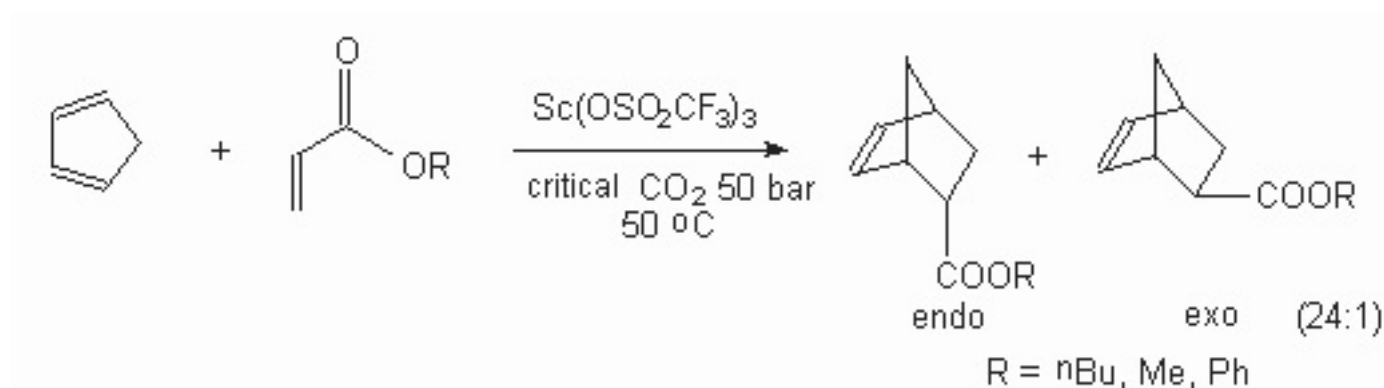
Other carbonyl compounds also enter into this reaction.



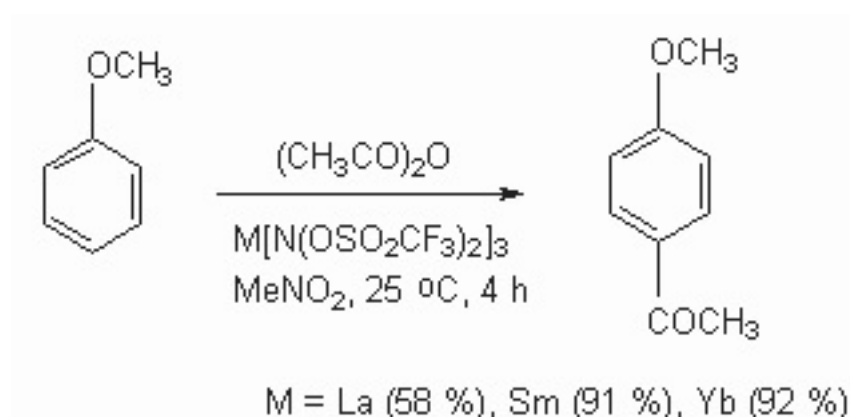
The nature of Lewis acid element is important, affecting the reaction velocity.



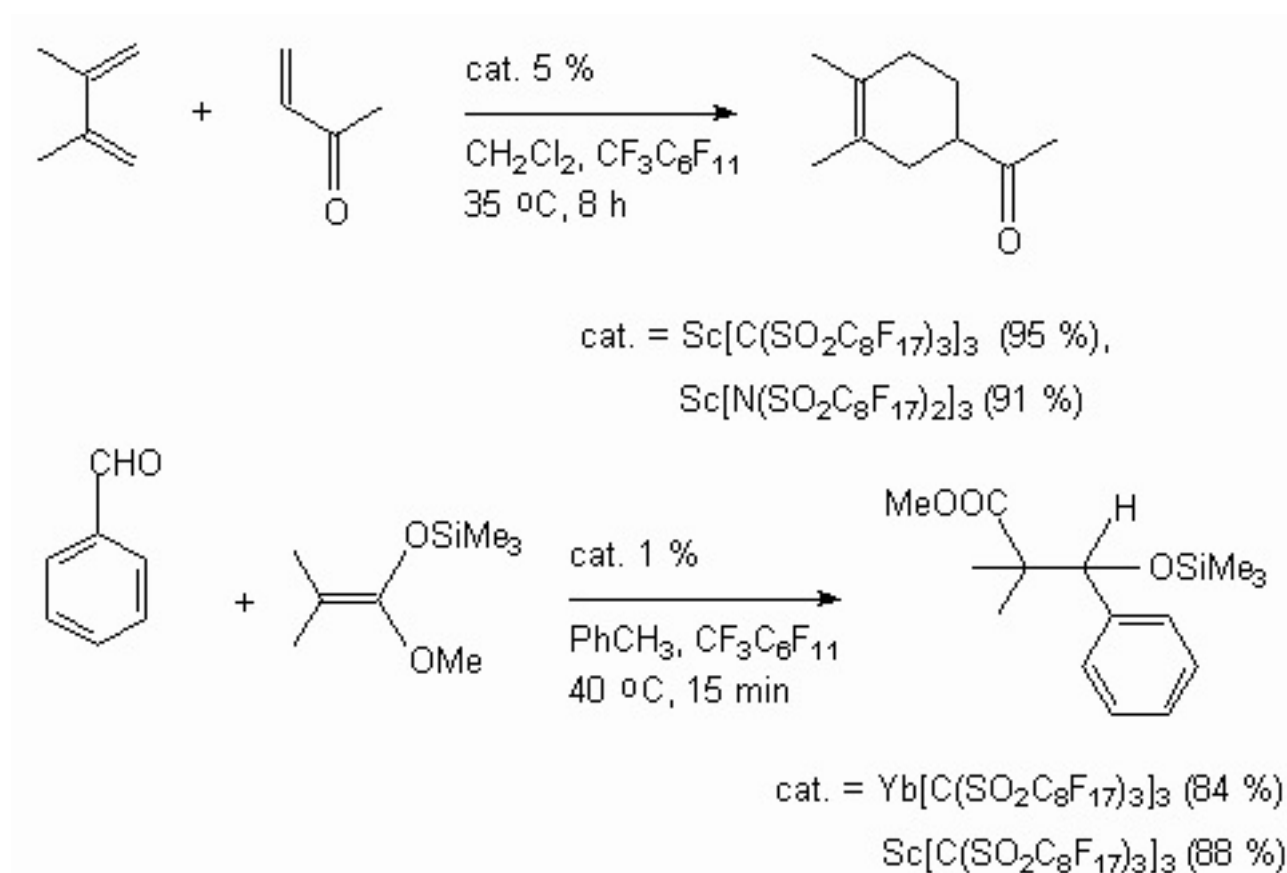
Trifluoromethanesulfonates of scandium catalyses the reaction of Diels-Alder between different acrylates and cyclopentadiene in supercritical CO<sub>2</sub>. The reaction passes in a stereo-selective way [126].



Acylation of aromatic compounds is catalysed by bis- (trifluoromethanesulfonyl)amides of lanthanum, samarium and ytterbium [127a,b]. At this the present catalysts appeared to be more effective compare to trifluoromethanesulfonates of these elements [128].

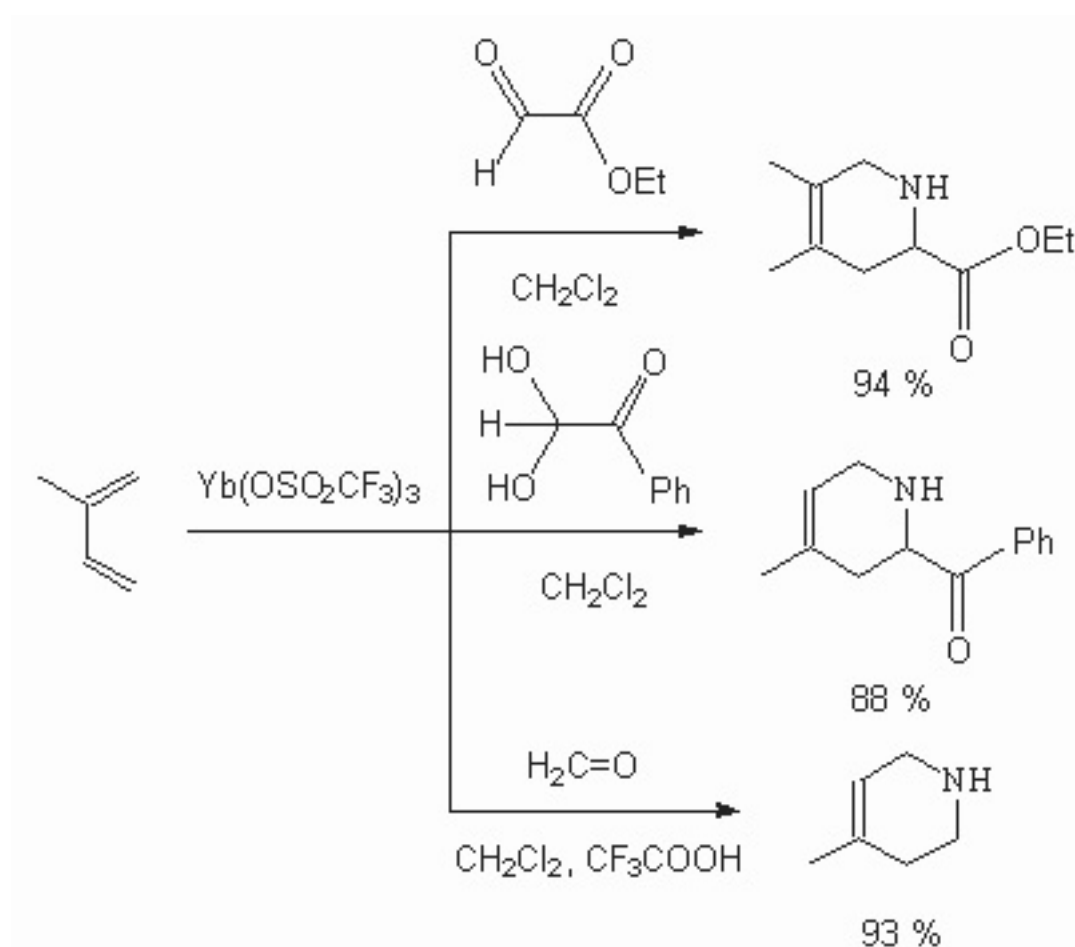


Tris(perfluorooctylsulfonyl)**methidine** of lanthanum and bis(perfluorooctylsulfonyl)amide of lanthanum are not only effective catalysts of alcohols and aromatic compounds acylation, but they are used as Friedel-Crafts catalysts of Diels-Alder reactions.



Instead of organic solvents supercritical carbon dioxide was used for these processes [130].

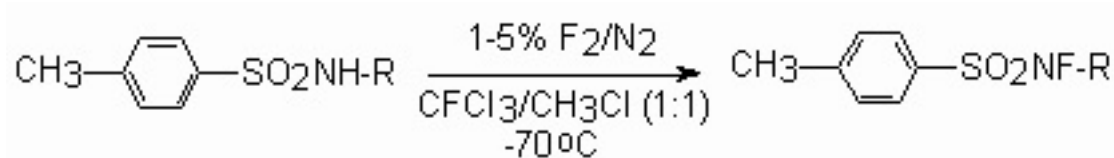
Diels-Alder reaction of different dicarbonyl compounds and 1, 2 - dienes passes with high yield in mild conditions when using ytterbium trifluoromethanesulfonate as catalyst [131].



### 3.4. Synthesis of N-F-containing compounds.

N-Derivative of bis-(trifluoromethanesulfonyl)imide is an effective fluorinating agent for aromatic compounds [132]. The reviews regarding synthesis of compounds, containing N-F bonds, and their use in organic synthesis you can find in [133,134].

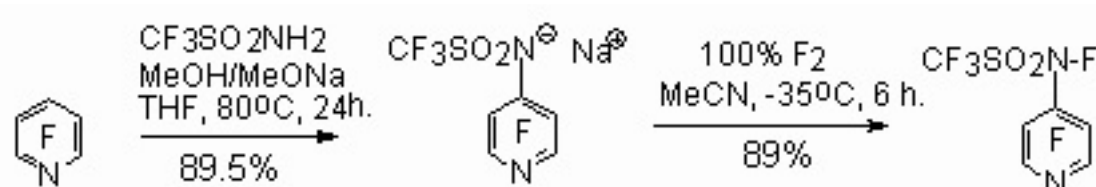
During fluorination of N-alkylsulfonamides in the  $\text{CFCl}_3$  -  $\text{CHCl}_3$  system using fluorine [135] ,  $\text{CH}_3\text{OF}$ [136] or  $\text{CF}_3\text{OF}$ [137,138] the corresponding N-fluoroderivatives are obtained.



R	Me	But	neopentyl-	<b>exo-2-nonbornyl</b>	endo-2-nonbornyl	cyclohexyl-
Yield, %	59	14	57	47	71	11

The fluorination of sodium salt of *N-tret*-butyl-*p*-toluenesulfonamide by cesium fluoro-oxy-sulfate in acetonitrile at 0-5°C give the *N*-fluoro-*N-tret*-butyl-*p*-toluenesulfonamide with high yield (69%) [139]. The fluorination of this substrate using elemental fluorine produces product only with the 14% yield [135].

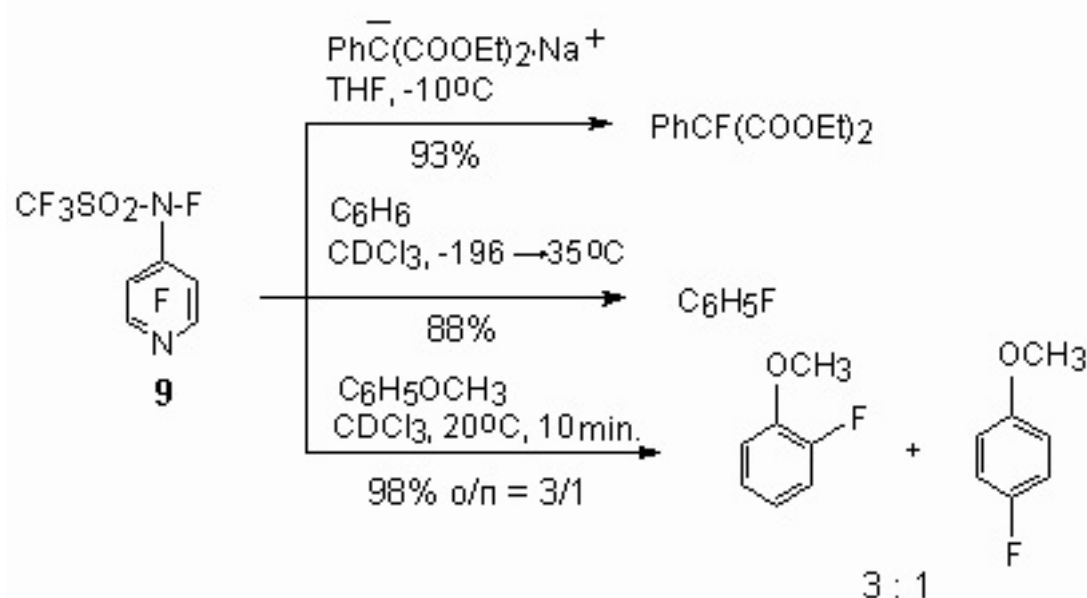
It is better to fluorinate sulfonamide derivatives in the form of corresponding salts. Thus, the fluorination of sodium salt of perfluoro *N*-(4-pyridyl)methanesulfoamide using elemental fluorine results in formation of *N*-fluoro-*N*-(4-pyridyl)methanesulfoamide [91,140].



The derivatives of sulfonamides having perfluoroquinolyl-, perfluoro-iso-quinolyl- substituents [137] are put into reaction.

The controlled fluorination of aromatic compounds using *N*-fluorolactams and *N*-fluorosulfonamides can be used for obtaining of a number of aromatic fluoroderivatives.

The fluoridation of organic compounds using *N*-fluorosulfonamides is described by many examples [136,140]. Thus, sulfonamides of **9** type fluorinate salts of malonic acid derivatives and aromatic compounds [135,140-146].



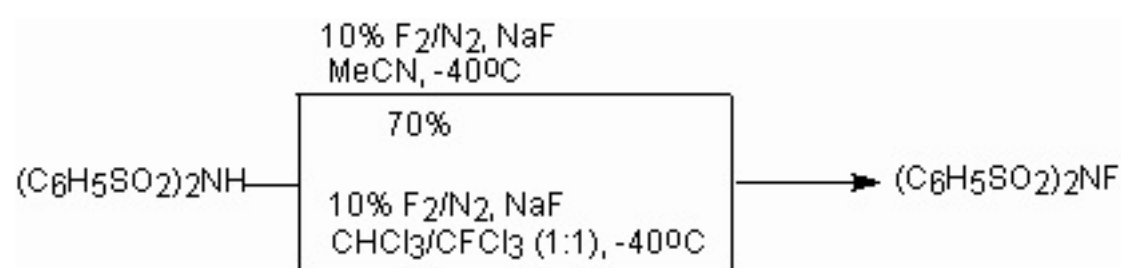
Obtaining methods of *N*-fluorodialkyl(aryl)sulfonimides are based on fluorination [ $\text{F}_2/\text{Ar}$  (1-3%) or  $\text{XeF}_2$ ] of corresponding dialkyl(aryl)sulfonimides. Base products are obtained with the yield up to 70% [137].

*N*-fluorosulfonimides  $(\text{CF}_3\text{SO}_2)_m\text{NFR}_n(\text{SO}_2\text{R}')_p$  (where  $m=1,2$ ;  $n,p=0,1$ ;  $\text{R}'$  - perfluoroalkyl, -cycloalkyl, -aryl) and  $\text{CF}_3\text{SO}_2\text{NF}(\text{SO}_2)_a\text{R}$  ( $a=0,1$ ) are obtained using fluorination of corresponding imides by elemental fluorine at -20°C [140-146]. Thus at  $\text{F}_2$  influence on  $(\text{CF}_3\text{SO}_2)_2\text{NH}$  at -20°C  $(\text{CF}_3\text{SO}_2)_2\text{NF}$  is formed with the yield 94,6% [140]. The synthesis of *N*-fluorosulfonimides using method is described in many works [147-149].

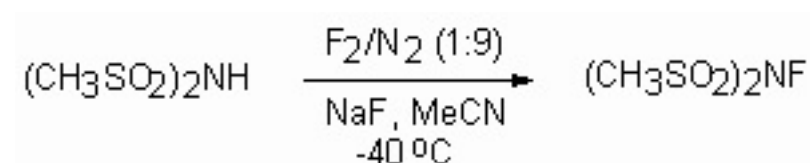
In the article [140]it is offered to use not amides of acids, but their lithium derivatives. Authors

used diluted elemental fluorine in non-polar solvents (  $\text{CHCl}_3$ ,  $\text{CFCl}_3$ , HF, fluorocarbon, MeCN) at 80-135°C in presence of solid phase ( $\text{NaF}$ ,  $\text{CaF}_2$ ) [140].

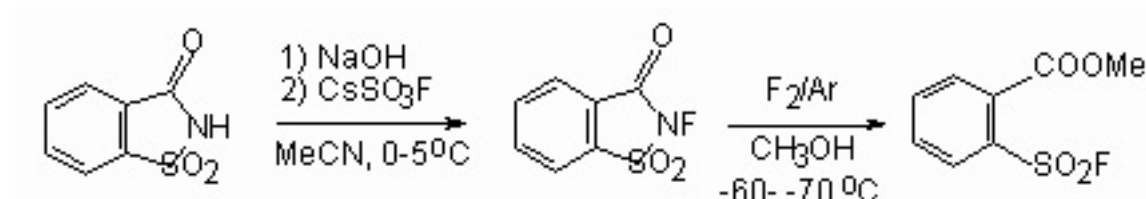
N-fluorodiphenylsulfonimide was obtained during fluorination of diphenylsulfonimide by fluorine (diluted nitrogen) in presence of sodium fluoride in acetonitrile at -40°C [150].



N-fluorodiphenylsulfonimide is a white crystal substance, dissoluble in plenty of organic solvents (ether, THF,  $\text{CH}_2\text{Cl}_2$ , MeCN,  $\text{C}_6\text{H}_5\text{CH}_3$ ), convenient in handling, non hydroscopic and stable for storage. N-fluorodimethylsulfonimide, another N-fluorodialkylsulfonimides  $[(\text{CH}_3(\text{CH}_2)_n\text{SO}_2)_2\text{NF}]$ ,  $n = 1-3$  and N-fluoro-[1,3,2]-dithiazine-1,1,3,3-tetraoxide was produced similarly[151]. Water or water mixture with organic solvent can be used as media. Best results are achieved with sodium salts of corresponding sulfonamides [152]. Thus, N-fluorodimethylsulfonimide is obtained at action of elemental fluorine ( $\text{F}_2/\text{N}_2 = 1:9$ ) in acetonitrile in presence of sodium fluoride at -40°C with the yield 90% [153].

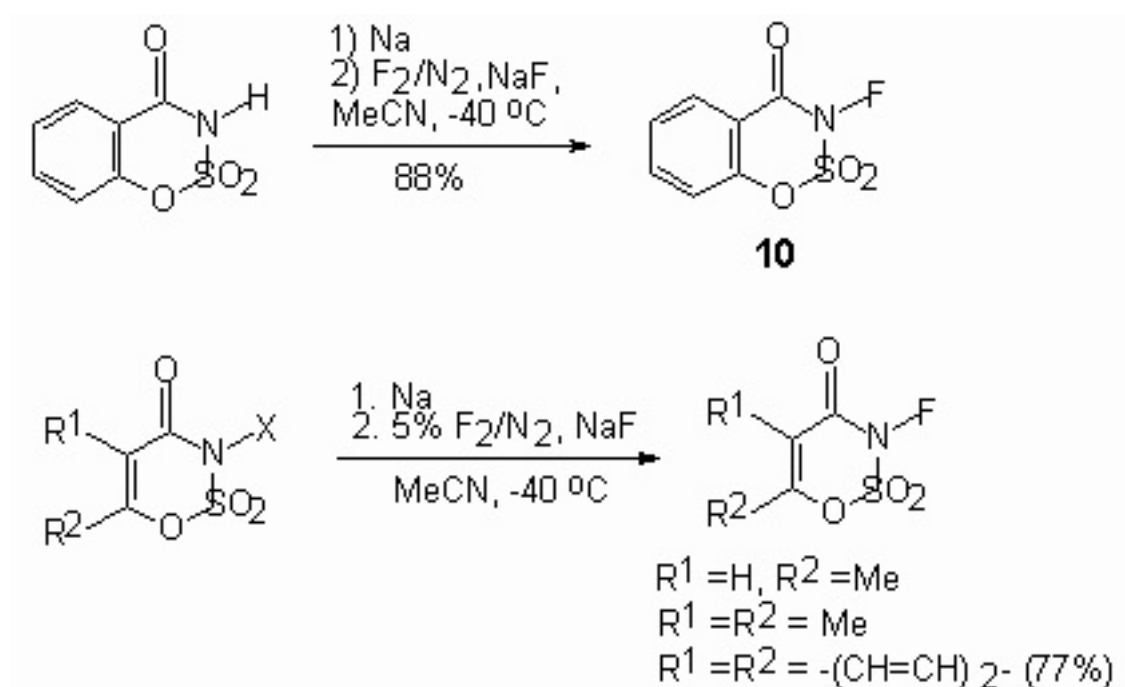


At fluorination of sodium saccharin salt by caesium fluoro-oxy-sulfate in acetonitrile at 0-5°C N-fluorosaccharin is obtained with the yield of 69%, while fluorine influence on this compound in methyl alcohol at -60 - -70°C results in uncovering of heterocycle and formation of o-fluorosulfonylmethylbenzoate (yield 28%) [154].

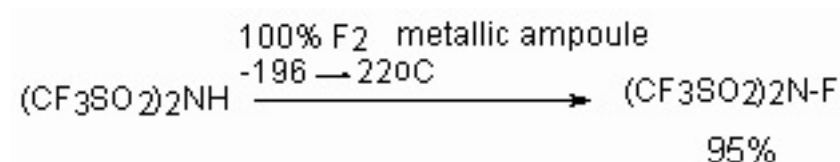


Fluorine-containing analogue of saccharine **10** is obtained by influence of diluted fluorine on sodium salt of benz-1,2,3-oxathiazine-4(3H)-one-2,2-dioxide in acetonitrile at low temperature in presence of sodium fluoride [155,156]. This reagent **10** is a crystal substance of sufficient stability and has a high capability for fluorination. Mainly it is used for fluorination of different salts, steroids and aromatic compounds.



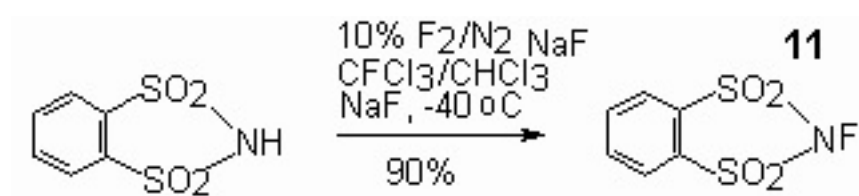


The most active agent among N-fluorosulfonimides is N-fluoro-bis-(trifluoromethanesulfonyl)amide, obtained according the above scheme with total yield 76% . This compound has a boiling point 90-91°C and is thermally stable, it can be kept in glass and is rather effective agent for fluorination with wide field of application [147-149].



Marked with isotope <sup>18</sup>F N-fluoro-bis-(trifluoromethanesulfonyl)amide is obtained according to the same scheme (radiochemical yield 45%) [157].

Stable white crystal powder of N-fluoro-o-benzenedisulfonimide **11** [158-160] is obtained by action of fluorine diluted by nitrogen upon o-benzenedisulfonimide at low temperatures.



N-F-containing compounds reveal high activity as fluorinating agents [161].

**to be continued**