

# 1,1-DIFLUORO-2(1H)-NAPHTHALENONES: SYNTHESIS, PROPERTIES AND APPLICATIONS

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Organofluorine compounds attract much attention in industry, pharmacology and materials design. Such an importance requires the development of effective methods of synthesis of organofluorine compounds based both on the incorporation of fluorine atoms in organic targets and use of fluorine-containing building blocks to construct more complex structures.

Our efforts in the development of effective fluorination methods are based on widely applicable direct electrophilic fluorination [1]. We have recently developed the solvent-free methodology for the fluorination of aromatic compounds with Selectfluor reagent. Combining solvent-free synthesis with vacuum sublimation to obtain products allows us to reach quite a low values of E-factor (3.7-5.7) [2]. The perspectives of using water and aqueous solvents as media for electrophilic fluorination was also demonstrated earlier [3].

We have found that easily obtained products of the electrophilic fluorination of various 2-naphthols – 1,1-difluoro-2(1H)-naphthalenones are promising fluorine-containing building blocks for the synthesis of complex organofluorine molecules. We've explored the reactivity of the abovementioned compounds in the Diels-Alder reaction with simple dienes and have investigated the solvent effects in reaction with model diene [4].

Synthetic applicability of 1,1-difluoro-2(1H)-naphthalenones in the Diels-Alder reaction was further demonstrated in the synthesis of condensed tetracyclic polyaromatic products – tetraphenones and substituted tetraphenes [5]. The latter was demonstrated to have relatively low values of HOMO-LUMO gap (3.0 eV) that makes it promising candidates to develop organic semiconductors.

This work was supported by the Russian Foundation for Basic Research, grants 16-33-00944, 18-33-00529.

## References

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## Transformation of polyfluoroorganyltrifluoroborates, $M[R_fBF_3]$ , without C-BF<sub>3</sub> cleavage

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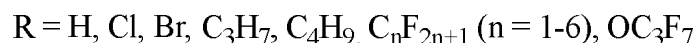
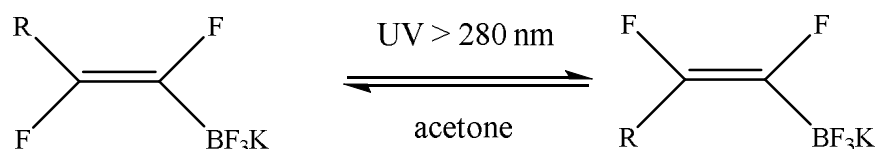
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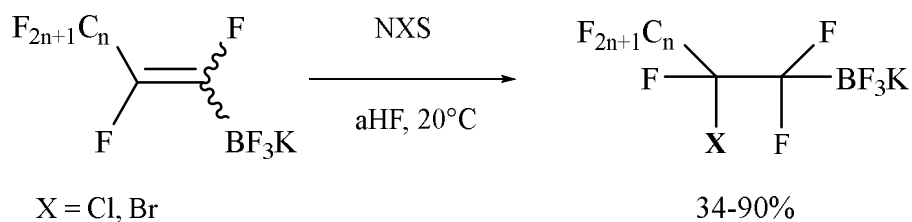
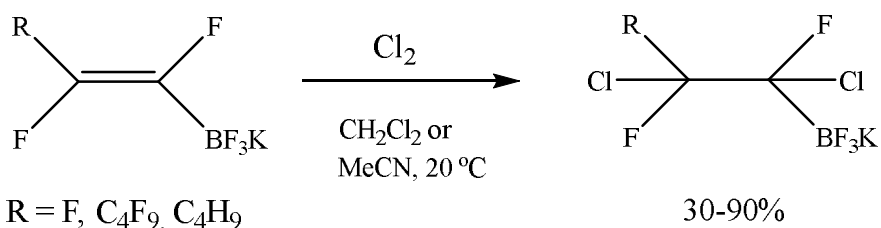
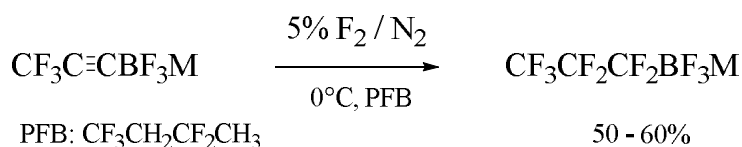
Polyfluorinated organyltrifluoroborates can be prepared by three ways: carbon-boron bond formation, re-functionalization at boron  $R_fBX_2$  to  $M[R_fBF_3]$  or  $M[R_fBY_3]$  to  $M[R_fBF_3]$ , and transformation of  $M[R'_fBF_3]$  to  $M[R_fBF_3]$ . Here the latter processes are reviewed.

### 1. Transformations of polyfluoroalkenyl- and alkynyl moiety in $M[R_fBF_3]$ .

#### a) Photoinduced cis/trans isomerization:

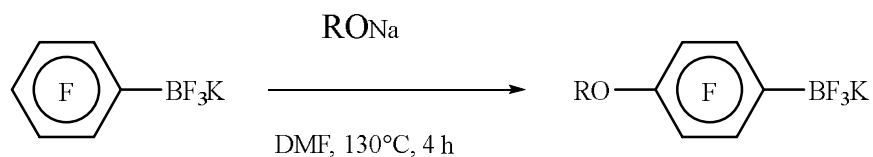


#### b) Addition of halogene and interhalogene across double or triple carbon-carbon bond:



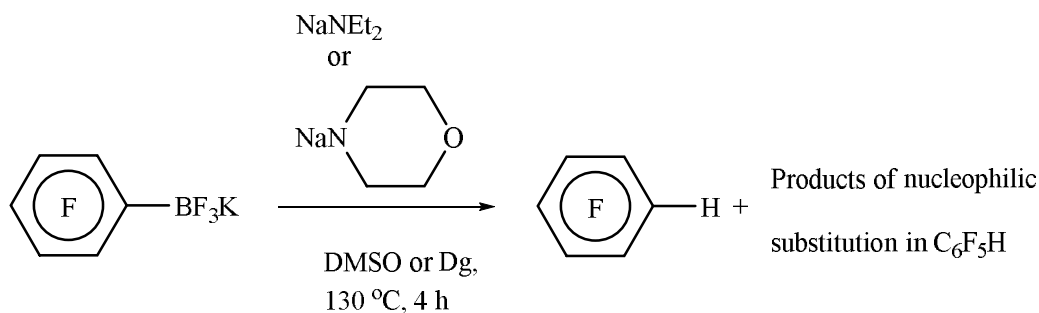
3. Nucleophilic substitution in pentafluorophenyl moiety.

a) With O-nucleophiles:

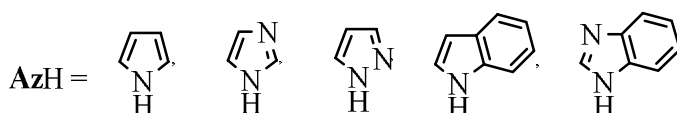
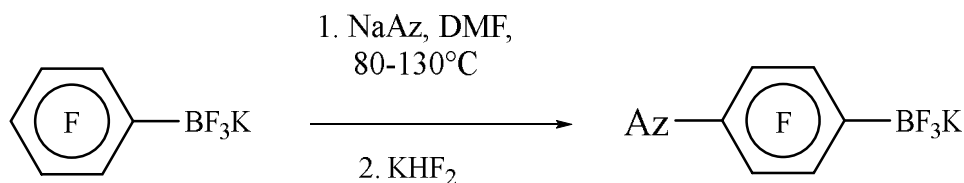


R = Alkyl, PhCH<sub>2</sub>, Ph, CH<sub>2</sub>=CHCH<sub>2</sub>

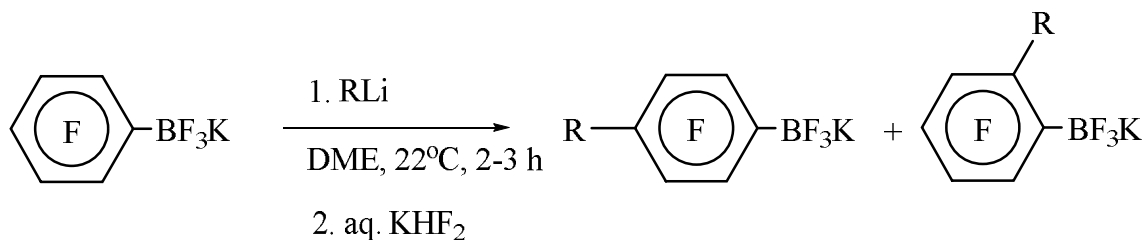
b) With N-nucleophiles:



Conversion < 10%



c) With C-nucleophiles:



R = CH<sub>3</sub>, C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>5</sub>

## DAIKIN'S BUSINESS OVERVIEW

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### 1. Introduction to Daikin Industries

Daikin Industries has two businesses, machinery with a focus on air conditioning and chemicals. This time, I introduce the Daikin's history, business introduction and business contents of the chemistry division.

### 2. Attractiveness and Applications of Fluorinated Materials

The history of the development and industrialization of fluorinated resins, which began with the discovery of DuPont in 1938 and Plankett's PTFE(Polytetrafluoroethylene), is similar to that of other engineering plastics, but it is being actively developed for a variety of applications, and the industrialization of new materials continues. This is because fluorinated materials have many unique functions, and fluorinated materials have been attracting attention as an indispensable material in a variety of fields. In particular, it plays an important role in industry and in our daily lives in a variety of fields, including materials for semiconductor processes, materials for automobiles, and textile processing agents that take advantage of the properties of heat resistance, chemical resistance, weather resistance, non-adhesion, and water repellency.

### Unique properties of fluorine compounds



Examples of product development in these fields and synthetic intermediates derived from TFE monomers are presented.

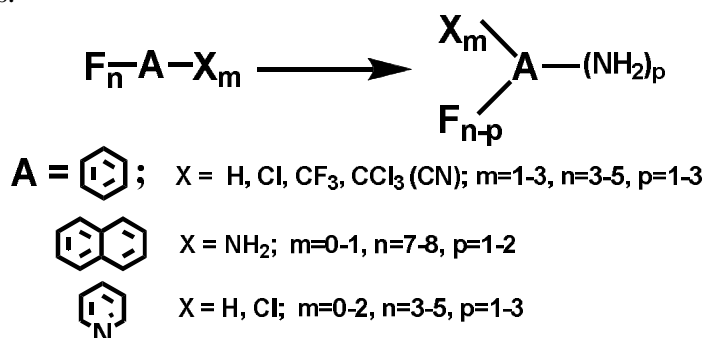
## Selective one-pot mono-, di-, and triaminodefluorination of polyfluoroarenes in anhydrous ammonia – the convenient and shortest route to monomers and building blocks for fluorinated polyimides and other hi-tech materials

T.A. Vaganova, E.V. Malykhin

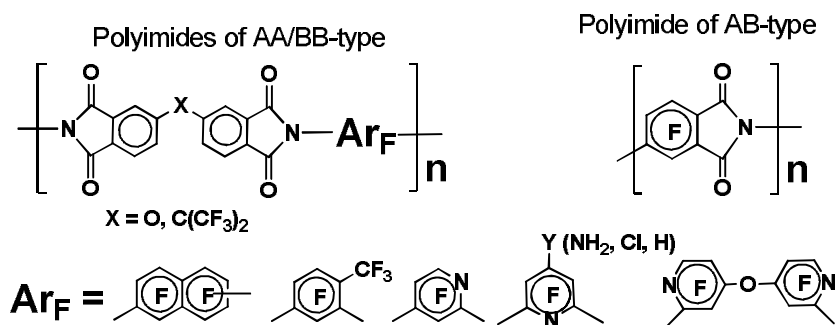
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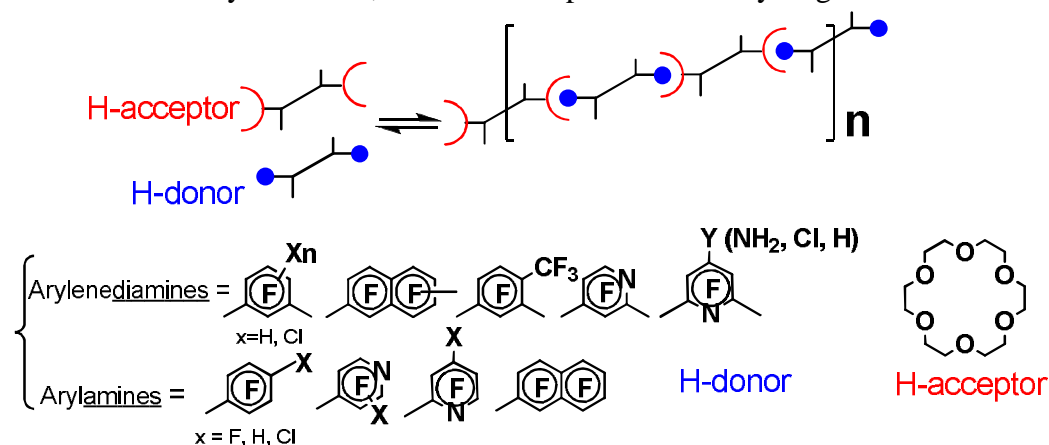
A technologically advanced and ecofriendly method of aminodefluorination of polyfluorinated benzenes [1a], naphthalenes [1b], and pyridines [1c] has been elaborated. The reaction proceeds effectively in the anhydrous liquid ammonia as the reagent and a solvent simultaneously; product yields achieve 85-95%. The specific temperature of the process allows a certain amount of amino groups to be selectively introduced. Products of the reactions, i.e. high purity polyfluoroaromatic mono- and diamines serves as building blocks and monomers in the synthesis of drugs, agricultural and veterinary formulations, polyfluoroaromatic polyimides, and molecular co-crystals.



Highly fluorinated aromatic polyimides have excellent optical performance (high transparency and low optical transmission losses in the near-IR and UV-vis regions), thermal stability (high glass transition and weight loss temperatures), good dielectric properties and high hydrophobicity. These characteristics determine their use in modern optoelectronic applications. We have developed technological methods for the preparation of highly fluorinated polyimides [2a], which became the basis for obtaining hi-tech materials, for example, transparent and thermostable matrixes for NLO materials [2b], modifiers-hardeners for epoxy insulating coatings [2c].



Organic cocrystals are a hot trend in the design of materials with nonlinear optical, photochromic, magnetic and electroactive properties. Solid-state transitions in a crystal under external action are used in thermal and photochromic molecular sensors, switches and molecular machines. Co-crystals serve as molecular containers for regio- and stereoselective reactions, as delivery systems for pharmaceutical ingredients *in vivo*, etc. We have synthesized and investigated the properties of the new objects for crystal engineering – associates of polyfluoroaromatic mono- and diamines and macrocyclic ethers, which form supramolecular hydrogen-bound assemblies [3a].



For a number of polyfluoroaromatic amines, there are found significant changes in the fluorescence characteristics due to the formation of associates with 18-crown-6 – build-up or quenching of the emission [3b]. These phenomena seems to be promising for using the organic cocrystals to make solid-state supramolecular chemospecific indicators and sensors.

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## Company Overview and Introduction of Some Fluoroorganic Materials in AGC

Yoshitomo Morizawa

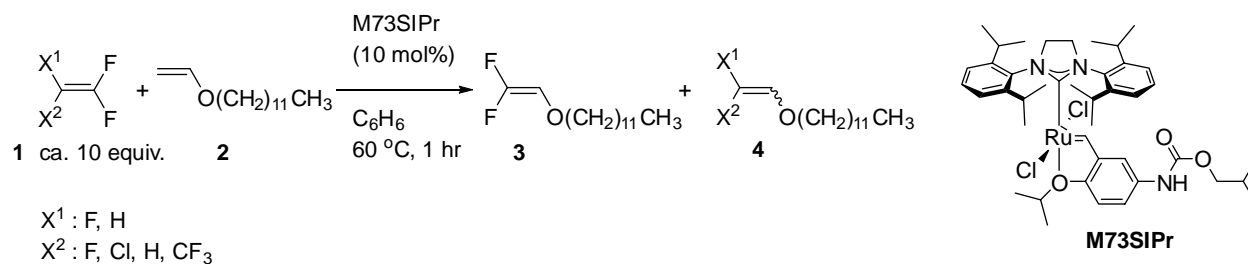
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AGC Inc. manufactures a variety of organofluorine products, which have been widely used in the industry as thermoplastics, elastomers, membranes, textile finishes, coatings, and functional materials, including pharmaceutical and agricultural agents, based on their unique combinations of properties [1].

Hydrogen fluoride, fluorine gas, and fluoro monomers as a fluorine source or a fluorinated building block are important raw materials in fluoro chemical industry. Here, first, unique fluorination method to produce perfluorinated compounds with fluorine gas, starting from hydrocarbon precursors is introduced. The method is applicable to a wide range of organic compounds and has a great advantage for synthesis of fluorine-containing molecules at will, simply by construction of the corresponding hydrocarbon skeleton [2].

Then, a successful ruthenium-catalyzed olefin cross-metathesis with fluoroolefins is demonstrated, although this has been considered to be difficult to perform by both theoretical and experimental precedents. Tetrafluoroethylene and the related fluoroolefins such as trifluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene are applicable to this transformation reaction [3].



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## Synthesis of SF<sub>5</sub>-Pyridines

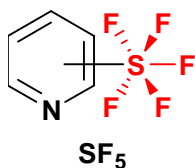
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Chemistry of SF<sub>5</sub>-substituted compounds has gained attention due to the unique property of SF<sub>5</sub>-group. Recent substantial efforts in synthetic SF<sub>5</sub> chemistry have made simple SF<sub>5</sub> aromatics easily available. However, the preparation of SF<sub>5</sub> pyridines remains a challenge (Fig. 1).

Unlike SF<sub>5</sub>-benzenes, which can be prepared at an industrial scale by direct fluorination of aryl disulfides or by Umemoto's procedure by the oxidative chloro-tetrafluorination of aryl disulfides to arene-sulfur chlorotetrafluorides (SF<sub>4</sub>Cl-arenes) followed by a chloride/fluoride exchange reaction with fluoride, heteroaromatic systems were difficult to follow this pathway and different strategies are used. In 2015, Dolbier and co-workers reported the first general method for the synthesis of *ortho*-SF<sub>5</sub>-substituted pyridines using Umemoto's method in which 2,2'-dipyridyl disulfides interacted with the KF/Cl<sub>2</sub>/MeCN system to afford SF<sub>4</sub>Cl pyridines. For further transformation of these sulfur chlorotetrafluorides to SF<sub>5</sub> pyridines, silver fluoride (AgF) was found to be the principal reagent. Despite this, *m*- and *p*-pyridine disulfides failed to form SF<sub>4</sub>Cl-pyridines under same conditions. Herein we disclose a general method for the preparation of *m*- and *p*-SF<sub>5</sub>-pyridines for the first time [1]. First, at least one fluorine atom in the pyridine ring effectively reduces the basicity of nitrogen, inhibiting it from entering a decomposition pathway. Second, fluorine induces greater stability of the SF<sub>4</sub>Cl moiety. Moreover, the C-F bond at the *ortho*-position of pyridine can be easily activated towards nucleophilic aromatic substitutions under suitable conditions selected.



**Fig. 1**

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(c) B. Cui, M. Kosobokov, K. Matsuzaki, E. Tokunaga, N. Shibata, *Chem. Commun.* **2017**, *53*, 5997;  
(d) B. Cui, S. Jia, E. Tokunaga, N. Saito, N. Shibata, *Chem. Commun.* **2017**, *53*, 12738;  
(e) P. Das, E. Tokunaga, N. Shibata, *Tetrahedron Lett.* **2017**, *58*, 4803.



## A new approach to fluorinated nitronyl nitroxides

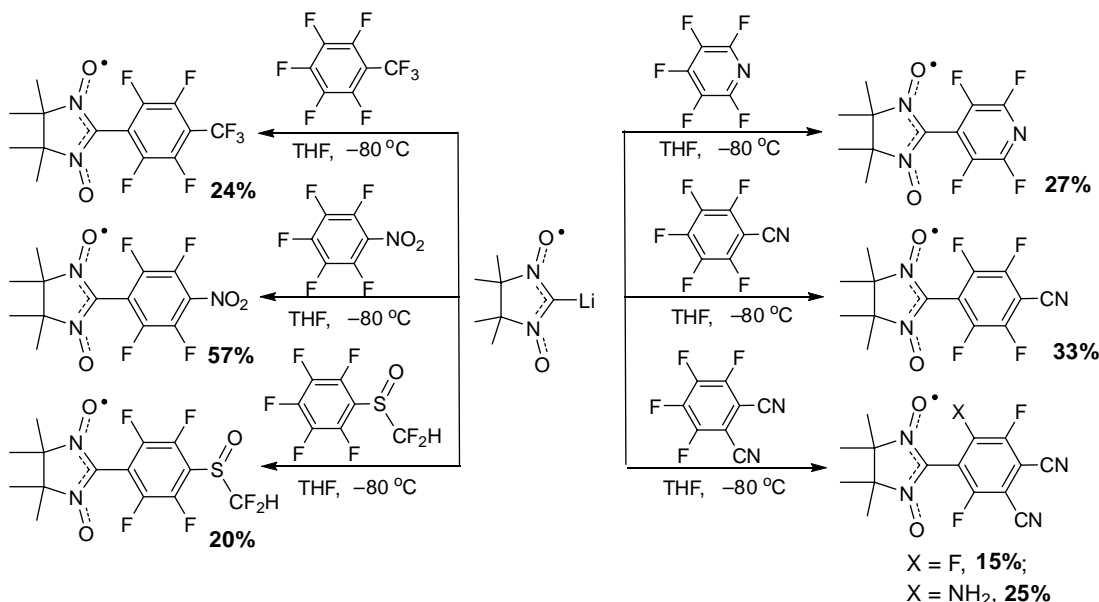
**Evgeny Tretyakov,<sup>1,2</sup> Pavel Fedyushin,<sup>1,2</sup> Borislav Koshcheev,<sup>1</sup> Alexander Maksimov,<sup>1</sup> Elena Panteleeva,<sup>1,2</sup> Irina Bagryanskaya,<sup>1,2</sup> Tatyana Rybalova,<sup>1,2</sup> Elena Zaytseva,<sup>1,2</sup> Elena Bagryanskaya<sup>1,2</sup>**

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Using nitroxide radicals to construct molecular magnets, spin labels, redox active materials, etc. stimulates the development of ways of their preparing. Recently it was shown that 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl lithium derivative (Li-NN) reacted with perfluorobenzonitrile to form 2-(4-cyanotetrafluorophenyl)-substituted nitronyl nitroxide [1]. To explore this approach, reactions of Li-NN with different polyfluoroarenes were investigated. As the result, new multifunctional fluorinated nitronyl nitroxides were prepared and completely characterized [2].



The proposed strategy can be useful for planning of the retrosynthesis of nitroxides bearing strong electron-withdrawing groups. Such paramagnetics arouse much interest in the field of molecular design of magnets; they can be used for creation of paramagnetic chemical sensors and organic rechargeable batteries.

### References

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### Acknowledgements

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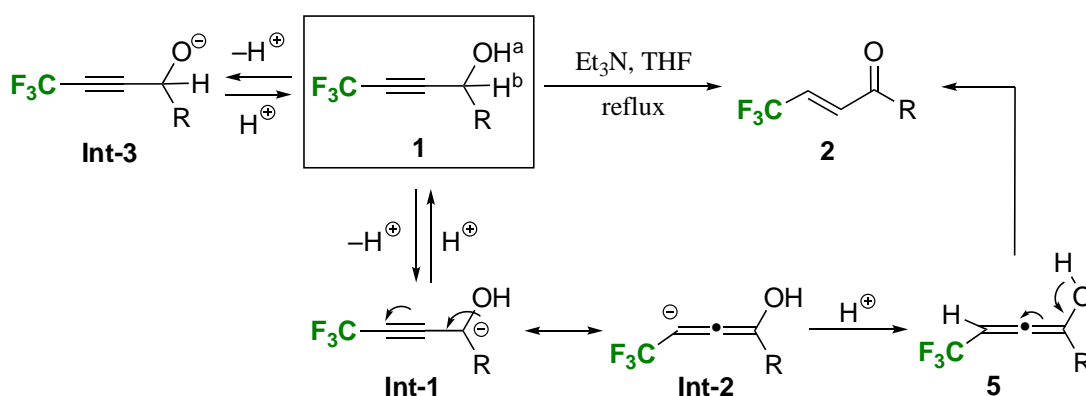
## Interesting Isomerization Reactions Initiated by the Abstraction of a Proton Activated by a CF<sub>3</sub> group

**Takashi Yamazaki**<sup>1</sup>

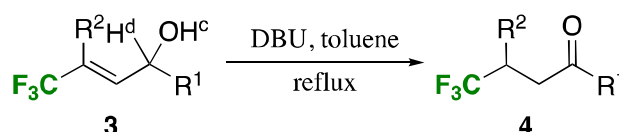
<sup>1</sup>*Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei 184-8588, Japan*

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Smooth isomerization of 4,4,4-trifluorinated propargylic alcohols **1** opened a new and convenient route to readily get access to the corresponding  $\alpha,\beta$ -unsaturated ketones **2** just by heating its THF solution at the reflux temperature in the presence of Et<sub>3</sub>N.<sup>[1]</sup> This reaction was considered to be initiated by the abstraction of H<sup>b</sup> in **1** and reprotonation occurred at the anionic site in **Int-2** to give **5** whose keto-enol isomerization afforded the desired products **2** in good to excellent yields. However, we at first thought that the deprotonation of H<sup>a</sup> would be the main path. Our computation on these transformations clarified that, contrary to our initial surmise, H<sup>b</sup> was more acidic than H<sup>a</sup> on the basis of the energetic difference between **Int-1** and **Int-3** ( $\Delta E=1.048$  kcal/mol when R=Me) and this difference became bigger when the R group was Ph ( $\Delta E=7.869$  kcal/mol when R=Ph). It is quite apparent that a CF<sub>3</sub> group plays a key role here because **Int-3** was found to be preferred by 7.803 kcal/mol when R=Ph and a CF<sub>3</sub> group was substituted for a CH<sub>3</sub> moiety.



Our computation also anticipated the similar isomerization starting from the allylic alcohols **3** due to a slight carbanion preference (0.321 kcal/mol when R=Ph) and this was experimentally the case, and **3** easily isomerized to **4** under the action of such a stronger amine base as DBU at toluene reflux. Utilization of optically active substrates (R<sup>1</sup>=Ph; R<sup>2</sup>=Ph, 4-MeOC<sub>6</sub>H<sub>4</sub>-, 4-FC<sub>6</sub>H<sub>4</sub>-) recorded a high stereoselectivity with up to >99% chirality transmission.



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# 1,1-DIFLUORO-2(1H)-NAPHTHALENONES: SYNTHESIS, PROPERTIES AND APPLICATIONS

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Organofluorine compounds attract much attention in industry, pharmacology and materials design. Such an importance requires the development of effective methods of synthesis of organofluorine compounds based both on the incorporation of fluorine atoms in organic targets and use of fluorine-containing building blocks to construct more complex structures.

Our efforts in the development of effective fluorination methods are based on widely applicable direct electrophilic fluorination [1]. We have recently developed the solvent-free methodology for the fluorination of aromatic compounds with Selectfluor reagent. Combining solvent-free synthesis with vacuum sublimation to obtain products allows us to reach quite a low values of E-factor (3.7-5.7) [2]. The perspectives of using water and aqueous solvents as media for electrophilic fluorination was also demonstrated earlier [3].

We have found that easily obtained products of the electrophilic fluorination of various 2-naphthols – 1,1-difluoro-2(1H)-naphthalenones are promising fluorine-containing building blocks for the synthesis of complex organofluorine molecules. We've explored the reactivity of the abovementioned compounds in the Diels-Alder reaction with simple dienes and have investigated the solvent effects in reaction with model diene [4].

Synthetic applicability of 1,1-difluoro-2(1H)-naphthalenones in the Diels-Alder reaction was further demonstrated in the synthesis of condensed tetracyclic polyaromatic products – tetraphenones and substituted tetraphenes [5]. The latter was demonstrated to have relatively low values of HOMO-LUMO gap (3.0 eV) that makes it promising candidates to develop organic semiconductors.

## References

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## Acknowledgements

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## Carbonylation of perfluorobenzocycloalkenes and their perfluoroalkyl and pentafluorophenyl derivatives in SbF<sub>5</sub> medium

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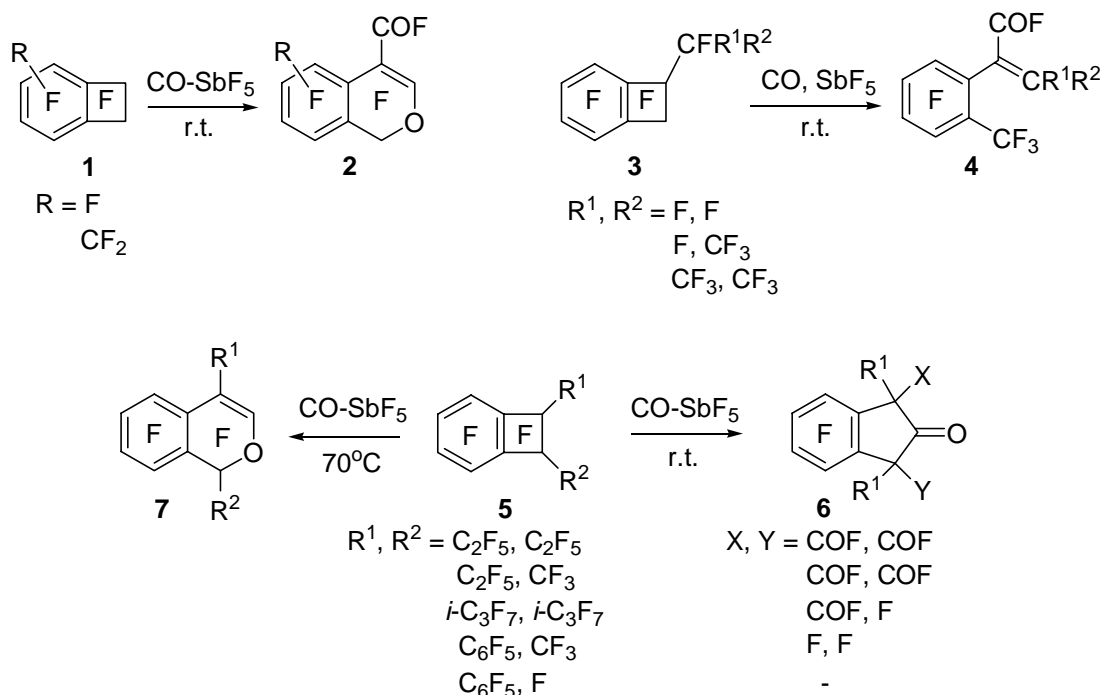
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We have found [1-3] that perfluorobenzocycloalkenes and a number of their perfluoroalkyl and pentafluorophenyl derivatives undergo carbonylation under the action of CO in the presence of SbF<sub>5</sub> and it is the first example of carbonylation of perfluorinated organic compounds. Most of these transformations readily proceed at room temperature and atmospheric pressure with complete conversion of starting compound, addition of more than one CO molecule occurs in a number of cases.

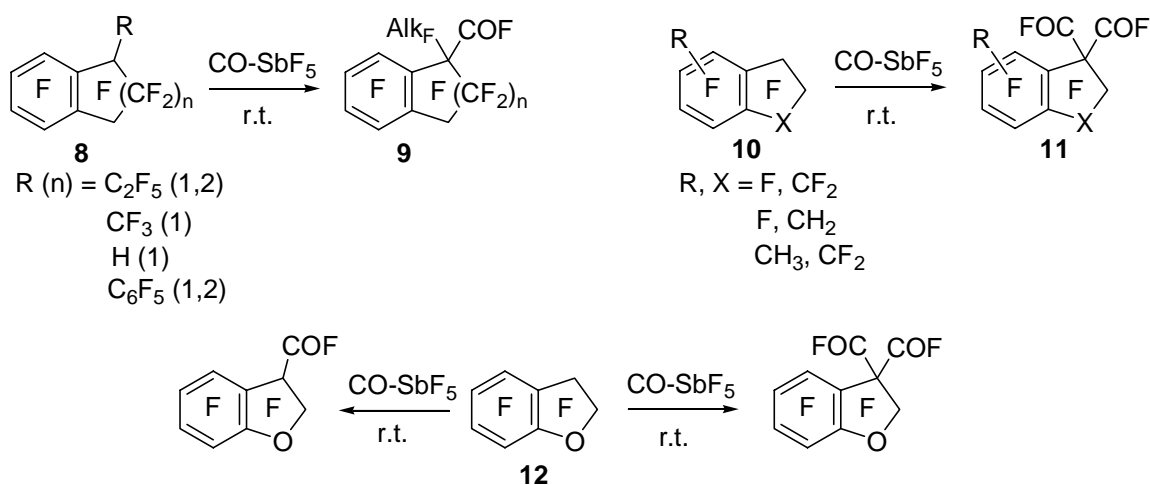
Perfluorinated benzocyclobutene derivatives in the CO–SbF<sub>5</sub> system undergo carbonylation/four-membered ring opening (or expansion) tandem reaction. Thus, perfluorobenzocyclobutenes (**1**) with unsubstituted aliphatic cycle adds two CO molecules to form isochromenes (**2**). Perfluoro-1-alkylbenzocyclobutenes (**3**) undergo monocarbonylation at the substituted position of the four-membered ring to form 2-(2-methylphenyl)alkenoic acid derivatives (**4**) [1].



1,2-Disubstituted perfluorobenzocyclobutenes (**5**) in the reaction with CO–SbF<sub>5</sub> at room temperature give indan-2-one derivatives (**6**) with or without fluorocarbonyl groups at the benzylic

positions. Increase in the reaction temperature up to 70°C leads to isochromenes (**7**) formations [2]. Carbonylation of perfluoro-1-phenylbenzocyclobutene also gives perfluoro-4-phenylisochromene [1].

Polyfluorinated indan and tetralin derivatives in the CO-SbF<sub>5</sub> system undergo carbonylation without transformation of the aliphatic ring. The degree of conversion varies in wide range and can reaches 100%. Thus, monosubstituted derivatives (**8**) of perfluorinated indan and tetralin undergo monocarbonylation at the substituted position of the aliphatic ring to give acyl fluorides (**9**). Polyfluoroindans (**10**) without the CFX fragment at the benzylic position give products of dicarbonylation to form indan-1,1-dicarbonyl difluorides (**11**). For perfluoro-2,3-dihydrobenzofuran (**12**), formation of both mono- and dicarbonylation products are possible depending on amount of antimony pentafluoride [3].



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