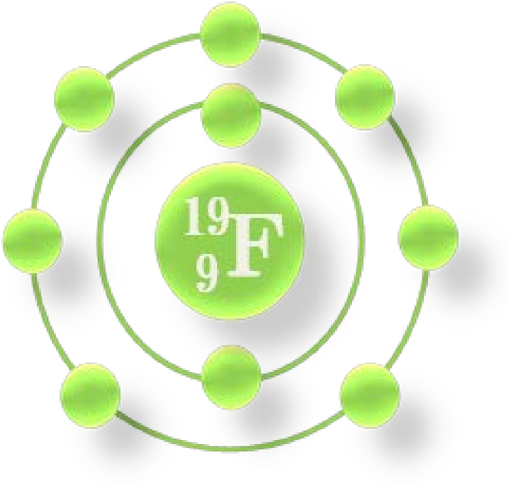
Japan/Russian Conference on Fluorine Chemistry and Friends 2014

Nagoya, Japan

December 8-10, 2014



Abstract

Department of Nanopharmaceutical Sciences

Nagoya Institute of Technology (NIT)

Program and Time Table

	December 8th 2014 (Monday)	December 9th 2014 (Tuesday)	December 10th 2014 (Wednesday)
Time Hall	To be announced	Bldg. 51	Bldg. 2, 11F, Lounge
9:30-10:00		Registration	
10:00-10:05		Opening remarks	
10:05-10:30		Lecture	Oral Session (10:00-10:20)
10:30-10:55		Lecture	Oral Session (10:20-10:40)
10:55-11:20		Lecture	Oral Session (10:40-11:00)
11:20-11:35		Coffee break (15 min)	Coffee break (20 min)
11:35-12:00		Lecture	Discussion (11:20-12:30)
12:00-12:25		Lecture	
12:25-12:50		Lecture	Lunch
12:50-14:10		Lunch (80 min)	
14:10-14:35		Lecture	End of conference
14:35-15:00		Lecture	
15:00-15:25		Lecture	
15:25-15:45		Coffee break (20 min)	
15:45-16:00		Lecture	
16:00-16:25		Lecture	
16:25-16:50		Lecture	
16:50-17:15		Lecture	
17:15-17:20		Closing remarks	
17:30-19:30	Welcome reception (18:00-20:00)	Banquet (120 min)	

Scientific Program (9th Tuesday)/ Lecture Hall: Bldg. 51

	Chairman	Lecture	Title
9:30-10:00		Registration	
10:00-10:05	Norio Shibata (Nagoya Institute of Technology)	Opening remarks (5 min)	
10:05-10:30		Takeo Taguchi (Sagami Chemical Research Institute, Tokyo University of Pharmacy and Life Science)	Fluorine Chemistry in Japan: A Brief History
10:30-10:55		Kazumasa Funabiki (Gifu University)	Organocatalytic in situ Generation of Trifluoroacetaldehyde from its Hemiacetal and Successive Aldol Reactions
10:55-11:20		Hideki Amii (Gunma University)	New Strategies for Aromatic Fluoroalkylation
11:20-11:35		Coffee break (15 min)	
11:35-12:00	Hideki Amii (Gunma University)	Tsunehiko Higuchi (Nagoya City University)	Synthetic Heme Thiolate Complexes as Precise Model of Cytochrome P450
12:00-12:25		Vladimir Boiko (INEOS)	Synthesis and Research of Reactivity of Organofluorine Silicon Derivatives
12:25-12:50		Toshiyuki Itoh (Tottori University)	Synthesis of gem-Difluoromethylene Building Blocks through Regioselective Allylation of gem-Difluorocyclopropanes
12:50-14:10		Lunch (80 min)	
14:10-14:35	Toshiyuki Itoh (Tottori University)	Sergey Osipov (INEOS)	α-CF3-Substituted Diazocompounds in Organic Synthesis and Catalysis

14:35-15:00		Michael Gerasimov (INEOS)	Structure and Phase Transitions in Polyphosphazenes with Fluorinated Side Groups
15:00-15:25		Takashi Ooi (Nagoya University)	Ion-Pairing in Ligand Design for Asymmetric Palladium Catalysis
15:25-15:45		Coffee break (20 min)	
15:45-16:00	Kenji Uneyama (Okayama University)	Norio Shibata (Nagoya Institute of Technology)	Novel Reagents for Electrophilic Pentafluorosulfanylphenylation of C, O, S and N-Nucleophiles
16:00-16:25		Sergey Igumnov (INEOS)	α-Fluoroalkylsilanes - A New Source of Unhydrated Fluorine Anion
16:25-16:50		Takashi Yamazaki (Tokyo University of Agriculture and Technology)	Novel Transformations of 4,4,4-Trifluorobut-2-yn-1-ol Initiated by Abstraction of the Propargylic Protons
16:50-17:15		Takahiko Akiyama (Gakushuin University)	Enantioselective Synthesis of Organofluorine Compounds by Means of Chiral Phosphoric Acid
17:15-17:20	Norio Shibata (Nagoya Institute of Technology)	Closing remarks (5 min)	
17:40-19:40		Banquet (Café Sala)	

Scientific Program (10th Wednesday)/Lecture Hall: Bldg. 2, 11F, Lounge

	Chairman	Oral Session	Title
10:00-11:10	Norio Shibata (Nagoya Institute of Technology (NIT))	Ibrayim Saydalim (NIT, and East China University of Science and Technology)	Efficient Synthesis of New-type Shelf-stable Reagents for Trifluoromethylation and Difluoromethylation Reactions
		Andrii Balia (NIT, and NAS of Ukraine)	Fluoroalkyl-Wrapped Push-Pull Porphyrins as Potential Dye-Sensitized Solar Cells
		Etsuko Tokunaga (NIT)	Bis(pentafluorosulfanyl)phenyl Azide as an Expeditious Tool for Click Chemistry toward Antitumor Pharmaceuticals
		Coffee break 10:30-10:40	
		Zhongyan Huang (NIT, and Beijing University of Chemical Technology)	To be announced
		Kohei Matsuzaki (NIT)	Introduction of Fluoro Aryl Group with Diaryliodonium Salts
		Satoru Mori (NIT)	Synthesis and Optical Property of Novel Phthalocyanine Dimers
11:10-11:20		Coffee break	
11:20-12:30		Discussion	
12:30-14:00		Lunch	
14:00-14:05		Closing remarks & End of conference	

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Takeo Taguchi, Professor Emeritus of Tokyo University of Pharmacy and Life Sciences, has been appointed as a senior adviser at Sagami Chemical Research Institute from 2012. Takeo Taguchi was born in 1947 in Sapporo, Japan. He received his B.S. degree in 1969 and his Ph.D. degree in 1974 from Tokyo Institute of Technology (TITEC) under the direction of Professor Teruaki Mukaiyama. He was then appointed as a Research Assistant at TITEC in 1974. He became a lecturer in 1976, an Associate Professor in 1983 and a Professor in 1989 at Tokyo University of Pharmacy and Life Sciences (formerly, Tokyo College of Pharmacy), where he joined Professor Yoshiro Kobayashi’s group from 1976 to 1989. He was a post-doctral fellow at University of California at Los Angeles (UCLA) with Professor D. J. Cram from 1981 to 1982. He is one of the editors of J. Fluorine Chemistry (Elsevier) responsible for Asian area. He has been working as the Chairman of JSPS 155th Committee from 2010 until 2015. He has published over 250 papers, patents and book chapters. His main interest is development of synthetic methods for organofluorine compounds.

Selected Publications

(1) Synthesis and Catalysis of Strong Carbon Acids Containing Bis(triflyl)methyl Group, Yanai, H., Taguchi, T., *J. Synth, Org. Chem. Jpn.*, **2014**, 72, 158-170.

(2) Preparation of (*Z*)-1-Fluoro-1-alkenyl Carboxylates, Carbonates and Carbamates through Chromium Mediated Transformation of Dibromofluoromethylcarbinyl Esters, Saito, A.; Tojo, M.; Yanai, H.; Wada, F.; Nakagawa, M.; Okada, M.; Sato, A.; Okatani, R.; Taguchi, T. *J. Fluorine Chem.*, **2012**, 133, 38-51.

(3) An Effective Method to Introduce Carbon Acid Functionality: 2,2-Bis(trifluoromethanesulfonyl)ethylation Reaction of Arenes, Yanai, H.; Ogura, H.; Fukaya, H.; Kotani, A.; Kusu, F; Taguchi, T., *Chem.–Eur. J.*, **2011**, 17, 11747-11751.

(4) Copper-free Defluorinative Alkylation of Allylic Difluorides through Lewis Acid-mediated C-F Bond Activation. Yanai, H.; Okada, H.; Sato, A.; Okada, M.; Taguchi, T., *Tetrahedron Lett.*, **2011**, 52, 2997-3000 (2011).

(5) Copper Mediated Defluorinative Allylic Alkylation of Difluorohomoallyl Alcohol Derivatives Directed to an Efficient Synthetic Method for (*Z*)-Fluoroalkene Dipeptide Isosteres, Watanabe, D.; Koura, M.; Saito, A.; Yanai, H.; Nakamura, Y.; Okada, M.; Sato, A.: Taguchi, T., *J. Fluorine Chem.*, **2011**, 132, 327-338.

(6) Highly Effective Vinylogous Mukaiyama–Michael Reaction Catalyzed by Silyl Methide Species Generated from 1,1,3,3-Tetrakis(trifluoromethanesulfonyl)propane, Takahashi, A.; Yanai, H.; Zhang, M.; Sonoda, T.; Mishima, M.; Taguchi, T., *J. Org. Chem.*, **2010**, 75, 1259-1265.

(7) Synthesis of 24,24-Difluoro- and 24ξ-Fluoro-25-hydroxyvitamin D_3, Kobayashi, Y.; Taguchi, T.; Terada, T.; Oshida, J.; Morisaki, M.; Ikekawa, N., *Tetrahedron Lett.*, **1979**, 2023-2026.

Fluorine Chemistry in Japan: A Brief History

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In this Conference I would like to describe a brief history of fluorine chemistry in Japan.

Before World War II (1941-1945), there was no remarkable outcome of fluorine chemistry from Japanese academia. Maybe, research activity on fluorine chemistry at academic institutions in Japan was initiated at the National Industrial Research Institute of Nagoya (at present National Institute of Advanced Industrial Science and Technology, so called AIST) in 1952, where major subjects were in analytical, organic and electrochemistry fields. At the same time, Kyoto University was the other platform for research activity, on mainly inorganic fluorine chemistry.

As the great founders of fluorine chemistry in Japan, following four University Professors should be noted, that is, Prof. Nobuo Ishikawa (Tokyo Institute Technology), Prof. Nobuatsu Watanabe (Kyoto University), Prof. Yoshiro Kobayashi (Tokyo College of Pharmacy) and Prof. Teiichi Ando (Kyoto University). Thanks to their devotional efforts, the first Fluorine Conference as a scientific meeting for the interchange of fluorine chemists was held in 1972. Since then this conference has been held annually, which is one of the most important activities of the Society of Fluorine Chemistry, Japan. The Society of Fluorine Chemistry, Japan was established in 2008 as a well-organized community for Japanese fluorine chemists belonging to both academia and industry, and of course the Society is one of the results based on the efforts by the founders and by the fluorine chemists who succeeded their will. Furthermore, for our activities both financial and technical supports from Japanese Government and Japanese Companies are acknowledged.

For Japanese, the 8th International Symposium on Fluorine Chemistry held in Kyoto in 1976 should be kept in their mind. I feel that the success of this international meeting was the real starting point for all Japan Fluorine Chemists being recognized worldwide and gathering together to build today’s fluorine chemists community.

The JSPS 155th committee founded by Prof. Nobuatsu Watanabe in 1990 and a historical story of some international relationships including Soviet-Japanese fluorine chemists Meeting organized by Prof. Nobuo Ishikawa firstly in 1979 will be introduced, although within as much as I know.

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Kazumasa Funabiki is an Associate Professor of Chemistry at Gifu University. He was born in 1967 in Osaka, Japan. He received a Ph.D. (1995) in chemistry from Kyoto Institute of Technology under the direction of Professors Hiroki Yamanaka and Takashi Ishihara. He found an academic position as an assistant Professor at Gifu University (Professor Katuyoshi Shibata) in 1995. He was an Alexander-von-Humboldt (AvH) fellow with Professor Dieter Enders at RWTH Aachen University (2000-2001). He got his promotion to an Associate Professor at Gifu University (Professor Masaki Matsui) in 2003. He received “Incentive Award in Tokai Branch in Synthetic Organic Chemistry, Japan (2004)” and “Ajinomoto Award in Synthetic Organic Chemistry, Japan” (2005). He has published around 150 papers, patents and book chapters. His current interests are not only synthetic fluorine chemistry but also functional dyes.

Selected Publications

(1) High Diastereoselectivity Induced by a Fluorous Alkyl Group in the Asymmetric Michael Reaction of Nitroalkenes Catalyzed by a Prolinol Methyl Ether, Funabiki, K.; Ohta, M.; Sakaida,Y.; Oida, K.; Kubota, Y.; Matsui, M. *Asian J. Org. Chem.* **2013**, *2*, 1048-1054.

(2) Design of NIR-Absorbing Simple Asymmetrical Squaraine Dyes Carrying Indoline Moieties for Use in Dye-Sensitized Solar Cells with Pt-Free Electrodes, Funabiki, K.; Mase, H.; Saito, Y.; Otsuka, A.; Hibino, A.; Tanaka, N.; Miura, H.; Himori, Y.; Yoshida, T.; Kubota, Y.; Matsui, M. *Org. Lett.* **2012**, *14*, 1246-124.

(3) Organocatalytic Asymmetric Direct Aldol Reactions of Trifluoroacetaldehyde Ethyl Hemiacetal with Aromatic Methyl Ketones, Funabiki, K.; Itoh, Y.; Kubota, Y.; Matsui, M. *J. Org. Chem.* **2011**, *76*, 3545-3550.

(4) Synthesis of a Novel Heptamethine-cyanine Dye for Use in Near-infrared Active Dye-sensitized Solar Cells with Porous Zinc Oxide Prepared at Low Temperature, Funabiki, K.; Mase, H.; Hibino, A.; Tanaka, N.; Mizuhata, N.; Sakuragi, Y.; Nakashima, A.; Yoshida, T.; Kubota, Y.; Matsui, M. *Energ. Environ. Sci.* **2011**, *4*, 2186-2192.

(5) Reversal of Diastereoselectivity in Reactions of the Trifluoroacetaldehyde Ethyl Hemiacetal with Enamines and Imines. Metal-free Complementary, *Anti-* and *Syn*-selective Synthesis of 4,4,4-trifluoro-1-aryl-3-hydroxy-2-methyl-1-butanones, Funabiki, K.; Matsunaga, K.; Gonda, H.; Yamamoto, H. Arima, T.; Kubota, Y.; Matsui, M. *J. Org. Chem.* **2011**, *76*, 285-288.

(6) Synthesis of Secondary α-Perfluoroalkyl- and Tertiary α,α-Bis(perfluoroalkyl)-*N*-methylprolinols and Their Catalytic Activities in the Acyl Transfer Reaction, Funabiki, K.; Shibata, A.; Hatano, K.; Matsui, M. *J. Fluorine Chem.* **2009**, 130, 444-448.

(7) Asymmetric Synthesis of β-Hydroxy-β-trifluoromethylated Ketones via In Situ Generation of Trifluoroacetaldehyde and its Asymmetric Carbon-carbon Bond Formation Reaction with Chiral Imines in Aqueous Media, Funabiki, K.; Hasegawa, K.; Murase, Y.; Nagaya, H.; Matsui, M. *J. Fluorine Chem.* **2006**, *127*, 545-547.

Organocatalytic in situ generation of trifluoroacetaldehyde from its hemiacetal and successive aldol reactions

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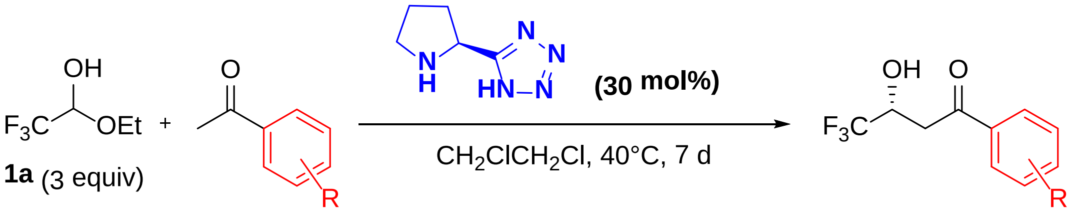
Trifluoroacetaldhyde (CF_3CHO) is especially the most attractive compound like fluorine-free aldehydes for the construction of α-trifluoromethylated aldol units. However it normally exists as a hemiacetal form due to the strong electron-withdrawing property of the trifluoromethyl group. Therefore, before the use of CF_3CHO, the aldehyde must be generated by the early protocols, which rely on not only using a large amount of conc H_2SO_4 but also utilizing a high reaction temperature. Recently, we have found that a stoichiometric amount of enamine or imine is capable to effective in situ generation of CF_3CHO as well as the successive carbon-carbon bond formation reaction under mild conditions, producing β-hydroxy-β-trifluoromethylated ketones in good yields. [1]

Here we would like to present that organocatalytic in-situ generation of trifluoroacetaldehyde from its hemiacetal and successive direct aldol reaction with some ketones affording β-hydroxy-β-trifluoromethylated ketones enantioselectively. [2]



References

[1] Funabiki, K. et. al. *Chem. Commun.* **1998**, 2051. *Synlett* **1999**, 1477. *J. Org. Chem.* **2003**, 68, 2853. *Chem. Commun.* **2004**, 2056. *"Fluorine-Containing Synthons"*, ACS Symposium Series 911: Soloshonok, V. A. Ed., Oxford University Press/ACS, Washington, D.C., **2005**, p 342. *J. Org. Chem.* **2011**, *76*, 285.

[2] Funabiki, K.; Itoh, Y.; Kubota, Y.; Matsui, M. *J. Org. Chem.* **2011**, *76*, 3545. Funabiki, K.; Yamamoto, H.; Nagaya, H.; Matsui, M. *Tetrahedron Lett.* **2006**, 47, 5507. For other groups, see. Torii, H.; Nakadai, M.; Ishihara, K.; Saito, S.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 1983. Nie, J.; Li, X.-J.; Zheng, D.-H.; Zhang, F.-G.; Cui, S.; Ma, J.-A., *J. Fluorine Chem.* **2011**, *132*, 468.

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Hideki Amii was born in Hyogo in 1968. He graduated from Kyoto University, where he received his Doctorate degree in 1996 under the direction of Prof. Yoshihiko Ito and Prof. Masahiro Murakami. During 1996-2003, he worked as Research Associate of the Department of Applied Chemistry, Faculty of Engineering, Okayama University (Prof. Kenji Uneyama's group). He carried out postdoctoral work in France with Dr. Guy Bertrand at Université Paul Sabatier during 2000-2001. In 2003, he was appointed to Associate Professor of Kobe University. In 2010, he moved to Gunma University, where he is currently Professor of Chemistry. He was the recipient of Inoue Research Award for Young Scientists (1998), Otsuka Award in Synthetic Organic Chemistry, Japan (1998), Award for Poster Contribution at the 13th European Symposium on Fluorine Chemistry, Bordeaux, France (2001), the Chemical Society of Japan Award for Young Chemists (2002), and Fluorine Chemistry Research Incentive Award (2010, from Research Foundation Itsuu Laboratory). His research interest focuses in the synthesis of organofluorine compounds by the use of metal reagents.

Selected Publications

(1) Highly Controlled Ring-Opening of Siloxydifluorocyclopropanes: A Versatile Route to Cyclic Fluoroketones, Y. Kageshima, C. Suzuki, K. Oshiro, H. Amii, *Synlett* **2015**, *26*, 63.

(2) Efficient Generation and Increased Reactivity in Cationic Gold *via* Brønsted Acid or Lewis Acid Assisted Activation of an Imidogold Precatalyst, J. Han, N. Shimizu, Z. Lu, H. Amii, G. B. Hammond, B. Xu, *Org. Lett.* **2014**, *16*, 3500.

(3) Formation and structure of a fluorinated [2.2]paracyclophan-1-ene, H. Amii, R. Hayashi, M. Seo, Y. Katahira, A. Kobayashi, K. Uneyama, *J. Fluorine Chem.* **2013**, *152*, 90.

(4) An Efficient Route to Difluoromethylated Pyridines, K. Fujikawa, A. Kobayashi, H. Amii *Synthesis* **2012**, *44*, 3015.

(5) Preparation, Structure, and Reactions of Trifluoroacetimidoyl Palladium(II) Complexes, H. Amii, K. Kageyama, Y. Kishikawa, T. Hosokawa, R. Morioka, T. Katagiri, K. Uneyama, *Organometallics* **2012**, *31*, 1281.

(6) A New Method for Aromatic Difluoromethylation: Copper-Catalyzed Cross-Coupling and Decarboxylation Sequence from Aryl Iodides, K. Fujikawa, Y. Fujioka, A. Kobayashi, H. Amii, *Org. Lett.* **2011**, *13*, 5560.

(7) Synthesis of 3,3,4,4-Tetrafluoro-1,2-bis(imino)cyclobutanes: A Cyclic Version of Fluorinated α-Diimines, H. Amii, M. Kohda, T. Katagiri, K. Uneyama, *J. Fluorine Chem.* **2006**, *127*, 505.

(8) A Rich Chemistry of Fluorinated Imidoyl Halides, K. Uneyama, H. Amii, T. Katagiri, T. Kobayashi, T. Hosokawa, *J. Fluorine Chem.* **2005**, *126*, 165.

(9) A Review of Mg Metal-Promoted C-F Bond Activation; A Reliable Synthetic Approach to Difluorinated Organic Compounds, K. Uneyama, H. Amii, *J. Fluorine Chem.* **2002**, *114*, 127.

(10) Reactions of Benzeneselenenyl Fluoride Generated by XeF_2-$(PhSe)_2$ System with Electron-deficient Alkenes, K. Uneyama, S. Hiraoka, H. Amii *J. Fluorine Chem.* **2000**, *102*, 215.

New Strategies for Aromatic Fluoroalkylation

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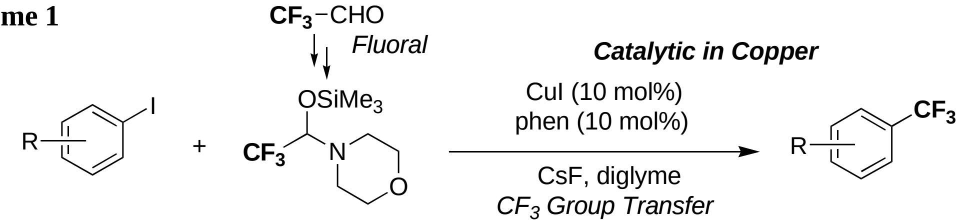
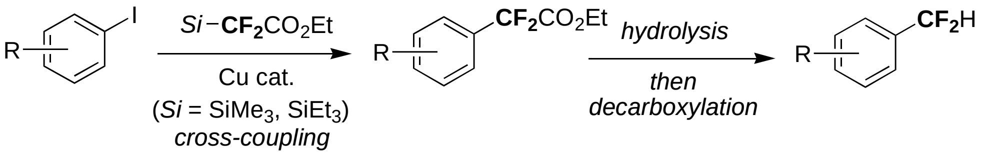
Trifluoromethylated aromatic compounds are the substances of considerable interest in various industrial fields. Owing to the increasing demands for fluoroaromatics, new methodologies for aromatic trifluoromethylation have been required from the viewpoints of cost, simplicity, efficiency, versatility, and environmental benignity including a catalytic process.[1] In 2009, we reported the first successful example of aromatic trifluoromethylation using a diamine ligand which makes possible a reaction catalytic in copper.[2] Herein, we show catalytic aromatic trifluoromethylation *via* β-carbon elimination. Fluoral (trifluoroacetaldehyde) and its derivatives are readily available compounds. Hemiaminals of fluoral are known to be convenient sources of trifluoromethyl anion.[3] We developed a catalytic procedure for aromatic trifluoromethylation by the use of trifluoroacetaldehyde hemiaminal derivative **1** as a cross-coupling partner (Scheme 1).[4]

Scheme 1



Compared with the chemistry of trifluoromethylation, that of difluoromethylation has been much less studied.[5] We disclosed a convenient cross-coupling/decarboxylation sequence leading to an efficient synthesis of difluoromethylated aromatics (Ar-CF_2H) *via* 2-aryl-2,2-difluoroacetates (Scheme 2).[6]

Scheme 2



References

(1) (a) O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, *111*, 4475. (b) Jin, Z.; Hammond, G. B.; Xu, B. *Aldrichimica Acta* **2012**, *45*, 67. (c) T. Liang, C. N. Neumann, T. Ritter, *Angew. Chem. Int. Ed.* **2013**, *52*, 8214.
(2) M. Oishi, H. Kondo, H. Amii, *Chem. Commun.* **2009**, 1909.
(3) T. Billard, B. R. Langlois, G. Blond, *Tetrahedron Lett.* **2000**, *41*, 8777.
(4) H. Kondo, M. Oishi, K. Fujikawa, H. Amii, *Adv. Synth. Catal.* **2011**, *353*, 1247.
(5) Xu, P.; Guo, S.; Wang, L.; Tang, Pingping *Synlett* **2015,** *26*, 36.
(6) (a) Fujikawa, K.; Fujioka, Y.; Kobayashi, A.; Amii, H. *Org. Lett.* **2011**, *13*, 5560. (b) Fujikawa, K.; Kobayashi, A.; Amii, H. *Synthesis* **2012**, *44*, 3015.

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Tsunehiko Higuchi is Professor of Chemistry at the Nagoya City University. He was born in 1956 in Sendai, Japan. He received a Ph.D. (1986) from The University of Tokyo (Professor Masaaki Hirobe). He worked at The University of Tokyo with Professor Masaaki Hirobe as an Assistant Professor (1984-1996) and with Professor Tetsuo Nagano as an Associate Professor (1996-2000). He became a full Professor of Nagoya City University (2000). He received The Pharmaceutical Society of Japan Award for Divisional Scientific Promotions (2003).

Selected Publications

(1) "Effect of Helical Conformation and Side-Chain Structure on γ-Secretase Inhibition by β-Peptide Foldamers: Insight into Substrate Recognition" Yuki Imamura, Naoki Umezawa, Satoko Osawa, Naoaki Shimada, Takuya Higo, Satoshi Yokoshima, Tohru Fukuyama, Takeshi Iwatsubo, Nobuki Kato, Taisuke Tomita, Tsunehiko Higuchi *J. Med. Chem.*, **2013**, *56*, 1443-1454."Effective Chiral Discrimination of Tetravalent Polyamines on Single-DNA Compaction"

(2) Yuko Yoshikawa, Naoki Umezawa, Yuki Imamura, Toshio Kanbe, Nobuki Kato, Kenichi Yoshikawa, Tadayuki Imanaka, Tsunehiko Higuchi *Angew. Chem. Int. Ed.*, **2013**, *52(13)*, 3712-3716.

(3) "Manganese Salen Complexes with Acid-Base Catalytic Auxiliary: Functional Mimetics of Catalase" Yukinobu Noritake, Naoki Umezawa, Nobuki Kato, Tsunehiko Higuchi *Inorg. Chem.*, **2013**, *52*, 3653-3662

(4) "Nitrous Oxide Reduction-Coupled Alkene-Alkene Coupling Catalysed by Metalloporphyrin" Shunsuke Saito, Hiro Ohtake, Naoki Umezawa, Yuko Kobayashi, Nobuki Kato, Masaaki Hirobe, Tsunehiko Higuchi *Chem. Commun.*, **2013**, *49*, 8979-8981

(5) "Inhibition of γ-Secretase Activity by Helical β-Peptide Foldamers" Yuki Imamura, Naoto Watanabe, Naoki Umezawa, Takeshi Iwatsubo, Nobuki Kato, Taisuke Tomita, and Tsunehiko Higuchi *J. Am. Chem. Soc.*, **2009**, *131*, 7353-7359

(6) "Extreme rate acceleration by axial thiolate coordination on the isomerization of endoperoxide catalyzed by iron porphyrin: relevance to prostaglandin H_2 isomerase catalysis" Takehiro Yamane, Kohei Makino, Naoki Umezawa, Nobuki Kato, and Tsunehiko Higuchi *Angew. Chem. Int. Ed.*, **2008**, *47*, 6438-6440

(7) "Enhanced Catalase-like Activity of Manganese Salen Complexes in Water: Effect of Three-dimensionally Fixed Auxiliary" Yoritada Watanabe, Azusa Namba, Naoki Umezawa, Masatoshi Kawahata, Kentaro Yamaguchi and Tsunehiko Higuchi *Chem. Commun*. **2006**, *47*, 4958-4960

(8) "Unique Oxidation Reaction of Amides with Pyridine-*N*-oxide Catalyzed by Ruthenium Porphyrin - Direct Oxidative Conversion of *N*-Acyl-L-prolines to *N*-Acyl-L-glutamates" Rina Ito, Naoki Umezawa and Tsunehiko Higuchi *J. Am. Chem. Soc.*, **2005**, *127*, 834-835.

(9) "Mechanistic Studies on the Binding of Nitric Oxide to a Synthetic Heme-thiolate Complex Relevant to Cytochrome P450" Alicja Franke, Grayna Stochel, Noriyuki Suzuki, Tsunehiko Higuchi, Kimiko Okuzono and Rudi van Eldik *J. Am. Chem. Soc.*, **2005**, *127*, 5360-5375.

Synthetic Heme Thiolate Complexes as Precise Model of Cytochrome P450

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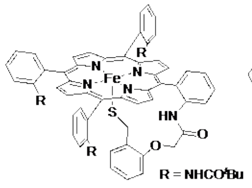
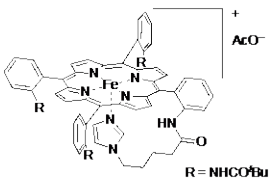
Cytochrome P450 plays a central role in drug metabolism and steroid biosynthesis. Among heme enzymes, cytochrome P450 and NO synthase (NOS) have strong oxidizing ability and unusual structure, in that their heme iron has thiolate coordination.

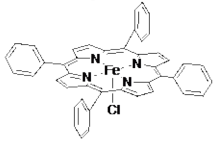
We previously succeeded in synthesizing the first synthetic heme thiolate (**SR** complex) which retains thiolate coordination during catalytic oxidation. We report here the synthetic heme-thiolate complex-catalyzed isomerization of an endoperoxide (EP) and the large enhancing effect of the thiolate ligand on the reaction. Prostaglandin H_2 (PGH_2) isomerase is a cytochrome P450-type endoperxide-isomerizing enzyme. It would be of interest to know why nature has selected the heme-thiolate structure for the isomerization of EP, among a wide repertoire of metal complexes. Reactions of **1**, which is a partial structure of PGH_2, with iron porphyrins were monitored by ^{1}H NMR measurement of samples obtained. In the presence of Fe(TPP)Cl or hemin dimethyl ester, **1** was completely unchanged in $CDCl_3$ at 25 ˚C for 24 h. In contrast, **SR** showed extremely high catalytic activity for EP isomerization/breakdown under the same conditions. Most of **1** was converted into malondialdehyde (**2**), ethylene (**3**), and epoxyaldehyde (**4**) within 10 sec.



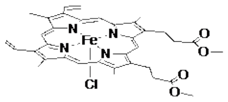
SR complex



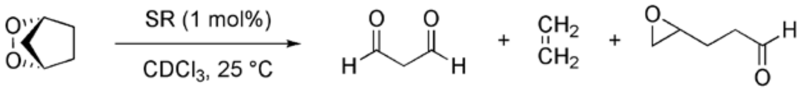
SR-Im



Fe(TPP)Cl



Hemin dimethyl ester



1 **2** **3** **4**

SR-Im complex, which is a mono-imidazole-ligated iron porphyrin, showed much lower activity than the **SR**. The initial rate of isomerization/breakdown by **SR** was almost *1,000-fold* higher than that by **SR-Im**. Coordination of chloride anion had no positive effect on the isomerization. This is the first example that axial ligand effect of thiolate on EP isomerization was unambiguously evaluated. Interestingly, the same type of conversion of **1** into **2** and **3** occurs in the reactions of PGH_2 and thromboxane synthase, prostacyclin synthase and cytochrome P450$_{CAM}$. The redox potential (Fe^{III}/(Fe^{IV} or the electronic isomer)) of **SR** was lower than those of the other complexes. This is also the first report of the redox potential (Fe^{III}/Fe^{IV}) of synthetic heme-thiolate. This ready accessibility of the high-valent iron form of heme thiolate is considered critical for O-O bond cleavage of EP, which has no active hydrogen.

Next, spin-trap experiments were carried out to examine the formation of radical species. Compound **1** was reacted with **SR** (2.5 mol%) for 0.5 sec at 25 ˚C in benzene and then 3,3,5,5-tetramethylpyrroline-*N*-oxide (TMPO) was added to the mixture. The ESR spectrum of the reaction mixture clearly showed a sextet signal assignable to an alkoxyl radical-derived product. This is the first direct evidence for formation of an oxy radical intermediate in the isomerization of EP catalyzed by heme.

We propose that the reaction mechanism of isomerization of EP by heme-thiolate is as follows. Rapid homolytic cleavage of the O-O bond of EP coordinated to the iron atom occurs with the assistance of the potent electronic “push effect” of the thiolate ligand. The biradical then splits to give products **2** and **3**. As another pathway, oxy-radical coordinated to heme can rearrange to afford unsymmetrical **4**.

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Vladimir Boiko is Research Assistant at A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences. He was born in 1988 in Voroshilovgrad, Ukraine. He graduated Ryazan State University named for S.Yeseni (2010). He has published 15 papers and 5 patents. He took part in International Symposium of Fluorous Technology as listener (2013). He took part in German-Russian-Ukraine Fluorine Symposium as speaker (2014). Занимается разботкой новых методов получения фторорганических соединений

Selected Publications

(1) Unusual reaction of (trifluoromethyl)trimethylsilane with natrium borane, Boiko V., Tyutyunov A.A, Igumnov S.M., Fluorine notes, **2011**, *#1*(74)
(2) Difluoromethylation of carbonyl compounds by (difluoromethyl)trimethylsilane, Boiko V., Tyutyunov A.A, Igumnov S.M., Fluorine notes, **2011**, *#5*(78)
(3) Reactions of (perfluoroalkyl)trimethoxyborate with electrophlic reagents, Boiko V., Tyutyunov A.A, Igumnov S.M., Ananiev V.A., Karnouhova K.A., Fluorine notes, **2012**, *#6*(85)
(4) Copper's perform in the synthesis of fluoroalkylsilanes at interaction of fluoroalkylhalogenides with silylation agent at the presence of zink-copper couple, Menshikov V.K., Boiko V., Tyutyunov A.A, Sterlin S.P., Igumnov S.M., Fluorine notes, **2012**, *#6*(85)
(5) Preparative method for higher fluoroalkylsilanes, Boiko V., Tyutyunov A.A, Don V.L., Igumnov S.M., Fluorine notes, **2013**, *#6*(91)
(6) Preparative method for polyfluoroaryltrimethylsilane, Boiko V., Tyutyunov A.A, Don V.L., Igumnov S.M., Fluorine notes, **2013**, *#6*(91)
(7) Production of pentafluorophenol by oxidation of trimethyl(pentafluorophenyl)silane, Boiko V., Tyutyunov A.A, Don V.L., Igumnov S.M., Fluorine notes, **2013**, *#6*(91)

Synthesis and Research of Reactivity of Organofluorine Silicon Derivatives

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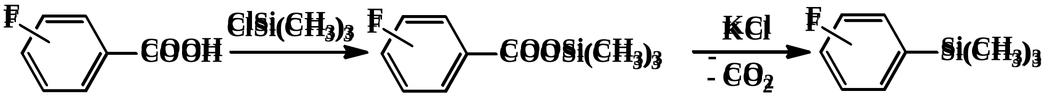
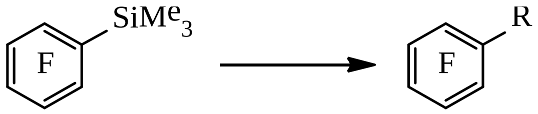
Element-containing fluoroalkyl derivatives are widely used in organic synthesis for the preparation of fluorine-containing compounds. Therefore, the development of new preparative methods of synthesis for element containing fluoroalkyl derivatives, used as fluoroalkylation reagents tailored to the conditions of industrial production, is an urgent goal for the organofluorine chemistry.

We have found that fluoroalkyl or aryl halides react with a number of silylating agents at Barbie reaction conditions in the presence of zinc-copper couple, obtained in situ, to give fluoroorganosilanes with preparative yield. We have discovered an unusual reaction of direct reduction of trifluoromethyl group in Ruppert's reagent. We have developed an original method for preparation of silicon containing fluoroaryl compounds by decarboxylation of trimethylsilyl esters corresponding fluoroaromatic acids. We have investigated the preparative methods for the synthesis of pentafluorobenzaldehyde, pentafluorostyrene and pentafluorophenol - valuable starting compounds in material science, medical and polymer chemistry.

$$R_FHal \quad + \quad RSiMe_3 \xrightarrow[Solv., \ T\ ^oC]{Zn/Cu} R_FSiMe_3$$

$$CF_3SiMe_3 \quad + \quad NaBH_4 \xrightarrow[Solv.]{} HCF_2SiMe_3$$





60-80%

R = OH, CHO, CH=CH$_2$

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Toshiyuki Itoh was born in Matsusaka City, Mie, Japan, in 1954. He graduated Tokyo University of Education in 1976. After working as a chemistry teacher in High Schools in his hometown (Mie prefecture), he decided to back to University and received his PhD in 1986 from the University of Tokyo. He was appointed as an Assistant Professor at Okayama University in 1987, then promoted to associate Professor in 1990. He worked with Professor Anthony G. M. Barrett as a visiting scholar at Colorado State University in 1990-1991 and moved to Tottori University in 2002, then, he was promoted to full professor in 2004.

He has published around 150 papers, 7 patents and 28 book chapters. He is the recipient of the Society of Synthetic Organic Chemistry Japan Award (2010), and The 8th Green and Sustainable Chemistry Award (2009). He is now serving the president of the Society of Fluorine Chemistry, Japan. His current research interests are development of new and useful synthetic methodologies based on Green Chemistry.

Selected five recent papers:

1) Synthesis of *gem*-Difluoromethylene Building Blocks through Regioselective Allylation of *gem*-Difluorocyclopropanes, Munemori, D.; Narita, K.; Nokami, T.; Itoh, T.* *Org. Lett.*, **2014**, *16*, 2638-2641.
2) Possible Means of Realizing a Sacrifice-free Three Component Separation of Lignocellulose from Wood Biomass Using an Amino Acid Ionic Liquid, Hamada, Y.; Yoshida, Y.; Asai, A.; Hayase, S.; Nokami, T.; Izumi, S.; Itoh, T.* *Green Chem*. **2013**, *15*, 1863-1868.
3) A Chronicle Review: Regioselective Synthesis of Trifluoromethyl Group Containing Allylic Amines using Palladium-catalyzed Allylic Amination Pathway, Hirakawa, T.; Kawatsura, M.*; Itoh, T.* *J. Fluorine Chem.*, **2013**, *152*, 62-69.
4) Ionic Liquid Engineering for Lipase-mediated Optical Resolution of Secondary Alcohols: Design of Ionic Liquids Applicable to Ionic Liquid Coated-Lipase Catalyzed Reaction, Abe, Y.; Yagi, Y.; Hayase, S.; Kawatsura, M.; Itoh, T.* *Industrial & Engineering Chemistry Research*, **2012**, *51*, 9952-9958.
5) Design of Cellulose Dissolving Ionic Liquids Inspired by Nature, Ohira, K.; Abe, Y.; Suzuki, K.; Mizuno, M.; Amano, Y.; Itoh, T.* *ChemSusChem.*, **2012**, *5*, 388-391.

Synthesis of *gem*-Difluoromethylene Building Blocks through Regioselective Allylation of *gem*-Difluorocyclopropanes

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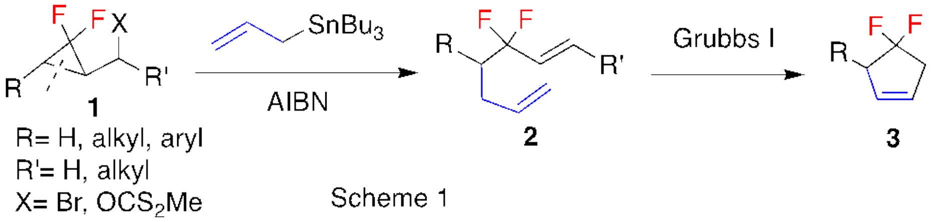
Much attention has been given to the preparation of *gem*-difluoromethylene derivatives as a source for novel functional materials [1]. Syntheses of *gem*-difluoromethylene compounds were generally achieved by the difluorination of carbonyl or thiocarbonyl functional group. However, fluorination reagents are limited and very expensive, hence, development of a synthetic strategy using a building block which has a *gem*-difluoromethylene moiety has also been recognized as a very attractive route to accessing *gem*-difluoromethylene compounds [1]. Dolbiers and co-workers reported that decomposition of the *gem*-difluorocyclopropane ring took place easily *via* a radical intermediate with a certain regioselectivity [2]. Inspired by their work, we attempted to prepare novel *gem*-difluoromethylene compounds through ring opening reaction of gem-difluorocycopropanes. We have thus established that *gem*-difluorocyclopropane deivatives **1** react with allyltributylstannane in the presence of 2,2'-azobis(isobutyronitrile)(AIBN) to afford 1,6-dienes **2** with a *gem*-difluoromethylene moiety at the allylic position. The reaction proceeds regioselectively with high yields and the 1,6-dinenes obtained are good precursors for cyclic systems containing a *gem*-difluoromethylene moiety. Furthermore, *S*-methyl carbonodithioate also works as a leaving group, rearrangement of the leaving group competes with the desired allylation, depending on the amount of allyltributylstannane. We next demonstrated a simple application of the ring-opening products **2**: The ring closing methathesis reaction took place smoothly and cyclopentene **3** was obtained in excellent yield when diene **2** was treated with 5 mol% of Grubbs catalyst (1st generation) (Scheme 1).



Scheme 1

[1] Ed. I. Ojima, "Fluorine in Bioorganic and Medicinal Chemistry", Wiley-Blackwell, London, UK (2009).
[2] Tian, F.; Bartberger, M. D.; W. R. Dolbier, Jr. *J. Org. Chem.* **1999**, *64*, 540-545.
[3] Munemori, D.; Narita, K.; Nokami, T.; Itoh, T. *Org. Lett.*, **2014**, *16*, 2638-2641.

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Sergey N. Osipov is head of laboratory of Ecological Chemistry at the A.N. Nesmeyanov Institute of Organoelement Compounds, RAS. He was born in 1960 in Zagorsk, USSR. He received a Ph.D. (1991) in chemistry from A.N. Nesmeyanov Institute of Organoelement Compounds under the supervision of Professor Alexey F. Kolomiets. He was granted a Postdoctoral Fellowship of Deutsche Academische Austauschdienst (DAAD, Germany) in the laboratory of Prof. Klaus Burger at Technical University of Munich (1993-1994). He worked at Leipzig University as leading research fellow on project “New fluorinated HIV-inhibitors” supported by Wolkwagen Stiftung (Germany, 1995-1997). He also acted as a visiting professor (1997 and 2001) at the University of Rennes (France). He received a Doctor of Science degree (habilitation) from A.N. Nesmeyanov Institute of Organoelement Compounds, RAS in 2002. In 2004 he was awarded by grant and diploma of Russian Foundation for Science Assistance in Nomination “Best Doctorates of Sciences under 45. He has published around 90 papers including 3 patents. His main current interest is synthetic organic and medicinal fluorine chemistry, organometallic chemistry and homogeneous catalysis.

Selected Publications:

(1) Access to Functionalized α-Trifluoromethyl-α-aminophosphonates via Intermolecular Ene-Yne Metathesis, I.M. Krylov, A.K. Mailyan, M.A. Zotova, C. Bruneau, P.H. Dixneuf, S.N. Osipov, *Synlett*, **2014**, 2624.

(2) Cu-Catalyzed Carbenoid Functionalization of Indoles by Methyl 3,3,3-Trifluoro-2-diazopropionate, I.E. Tsyshchuk, D.V. Vorobyeva, A.S. Peregudov, S.N. Osipov, *Eur. J. Org. Chem*., **2014**, 2480.

(3) Access to Cyclic α-CF_3-substituted α-Amino Acid Derivatives *via* Ring Closing Metathesis of Functionalized 1,7-Enynes, A.K. Mailyan, I.M. Krylov, C. Bruneau, P.H. Dixneuf, S.N. Osipov, *Eur. J. Org. Chem*., **2013**, 5353.

(4) Synthesis of CF_3-Containing 1,2,3,4-Tetrahydroisoquinoline-3-Phosphonates *via* Regioselective Ru-Catalyzed Co-cyclotrimerization of 1,7-Azadiynes, M.A. Zotova, D.V. Vorobyeva, P.H. Dixneuf, C. Bruneau, S.N. Osipov, *Synlett*, **2013**, 1517.

(5) Cyclobutene Ring-Opening of Bicyclo[4.2.0]octa-1,6-dienes: Access to CF_3-Substituted 5,6,7,8-Tetrahydro-1,7-naphthyridines, A.K. Mailyan, A.S. Peregudov, C. Bruneau, P.H. Dixneuf, S.N. Osipov, *J. Org. Chem*., **2012**, *77*, 8518.

(6) Synthesis of CF_3-containing tetrapeptide surrogates *via* Ugi reaction/dipolar cycloaddition sequence, D.V. Vorobyeva, N.V. Sokolova, V.G. Nenajdenko, A.S. Peregudov, S.N. Osipov, *Tetrahedron*, **2012**, *68*, 872.

(7) Synthesis of α-Trifluoromethyl-α-hydroxy Acid–Peptide Conjugates *via* Click Chemistry, N.V. Sokolova, D.V. Vorobyeva, S.N. Osipov, T.P. Vasilyeva, V.G. Nenajdenko, *Synthesis*, **2012**, 130.

(8) Synthesis of CF_3-containing α-alkynyl-α-aminophosphonates by Sonogashira cross-coupling reaction, M.A. Zotova, T.P. Vasilyeva, A.S. Peregudov, S.N. Osipov, *J. Fluorine Chem.*, **2012**, *135*, 33.

α-CF_3-Substituted Diazocompounds in Organic Synthesis and Catalysis

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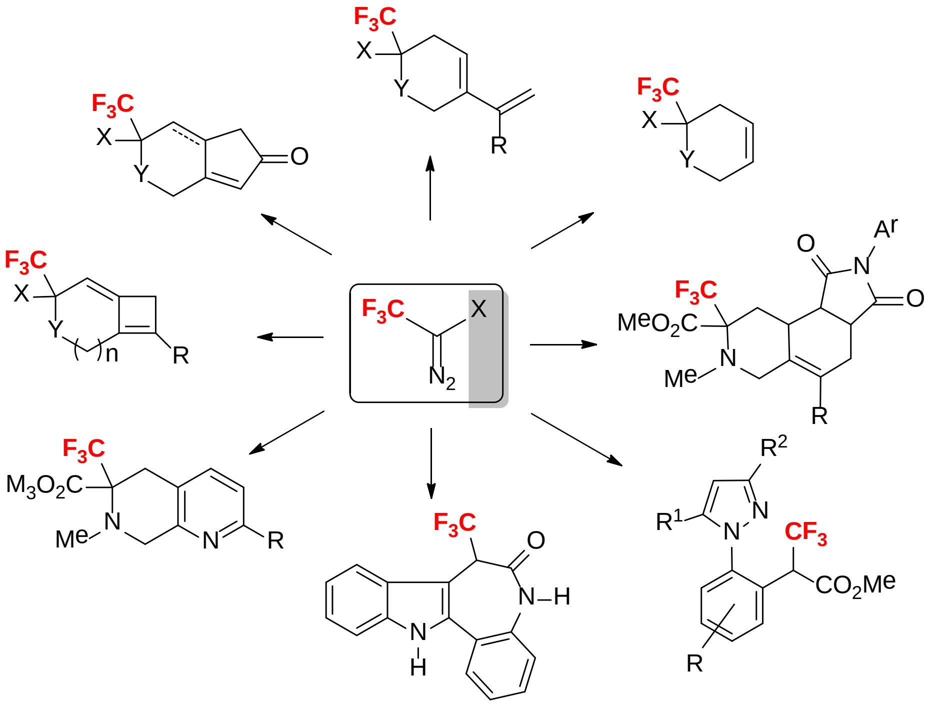
An efficient pathway to multifunctional CF_3-containing aromatic, heteroaromatic and heterocyclic compounds, including cyclic amino carboxylic and amino phosphonic acid derivatives have been developed. The method is based on *in situ* generation of highly electrophilic CF_3-carbene species from the corresponding α-diazo carboxylates or phosphonates under Cu- or Rh-catalysis and their reactions with appropriate nucleophilic partners.[1-4]



X = CO_2Me, P(O)$(OEt)_2$ Y = S, NMe

The further applications of the reaction products in metal-catalysed transformations of different types, *e.g.* such as ring closing diene and ene-yne metathesis, intramolecular Pauson-Khand reaction as well as [2+2]-cycloaddition, open an access to new families of fluorinated molecules.

1. D.V. Vorobyeva, A.K. Mailyan, A.S. Peregudov, N.M. Karimova, T.P. Vasilyeva, I.S. Bushmarinov, C. Bruneau, P.H. Dixneuf, S.N. Osipov, *Tetrahedron*, **2011**, *67*, 3524.
2. A.K. Mailyan, I.M. Krylov, C. Bruneau, P.H. Dixneuf, S.N. Osipov, *Synlett*, **2011**, 2321.
3. A.K. Mailyan, I.M. Krylov, C. Bruneau, P.H. Dixneuf, S.N. Osipov, *Eur. J. Org. Chem.*, **2013**, 5353.
4. I.E. Tsishchuk, D.V. Vorobyeva, A.S. Peregudov, S.N. Osipov, *Eur. J. Org. Chem.* **2014**, 2480.

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Michael Gerasimov is the Head of innovation policy and business development department at the Institute of Organoelement compounds RAS. He was born in 1965 in Moscow, Russia. He graduated from Moscow Lomonosov State University, Department of chemistry (1988) and received the Ph.D. (1994) in polymer chemistry from the Institute of Organoelement compounds of Russian Academy of sciences under the direction of Professor Vladimir Papkov. His research interests- Physics of Polymers: phase and relaxation transitions in polymers; structure and properties of mesomorphic polymers; (methods: DSC, WAXS, SAXS, mechanical measurements and microscope). He was a Member of Council of High-Molecular Compounds, participated in All-union and International Conferences, Seminars and Grants. Participated in joint projects with University of Ulm (Germany)
He has got 17 publications.

Since 1994 Michael Gerasimov has been involved into strategic business projects with Russian and international chemical companies. Analyzing of information about new perspective chemical technologies; identifying major trends in the chemical market.

Also he has More than 20 year experience in sales and marketing in the chemical industry in B2B both specialties and commodities chemicals, good knowledge and experience in export-import operations.

He was the Member of the Expert Council in the Budget Committee of State Duma of RF and Co-author of the manual “Customs Regulations in Russia”.

Now he deals with leadership and development wide international cooperation between business, industry and scientific centers, development of innovation policy and investment projects concept.

Structure and Phase Transitions in Polyphosphazenens with Fluorinated Side Groups

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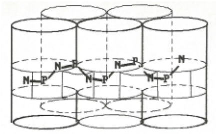
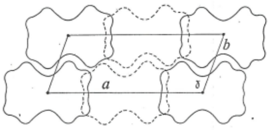
The structure and phase transitions in polyphosphazenes with different length fluorinated side groups

$$[N{=}P\ (OCH_2\ (CF_2)_x\ CF_2H)_2\ ]_n\ ;\ x=1,\ 3,\ 5$$

have been studied by DSC, x-ray diffraction….Two crystalline phases I and II and one mesomorphic phase III are founded. These phases convert reversibly one into the other on heating and cooling. Crystalline phase is characterized by monoclinic unit cell (with the parameters for $[N{=}P\ (OCH_2\ (CF_2)\ CF_2H)_2\ ]_n$ a=24.4 Å, b=9.96 Å, c=4.96 Å, $\gamma=123^o$).





The axes of both chains, traversing the unit cell, are directed along the "c" axis, the main chains having cis-trans conformation. Phase I is common crystalline structure for the main and side chains. With increasing temperature the samples exhibits phase transitions caused by changes in the packing of both main chains and side chains of macromolecules

The structure of Phase II is controlled mainly by packing of the side chains. Transition of Phase II into mesomorphic Phase III is accompanied with distortion of packing of the side chains. Mesomorphic Phase III is stable up to the degradation temperature of the polymers.

A significant effect of stress on the Phase II-III transition in oriented samples was found.

The conditions of preparation and the thermal prehistory of the copolymer films have a very strong effect on their mechanical properties on uniaxial drawing.

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Takashi Ooi was born in 1965 in Nagoya, Japan. He received his Ph.D. (1994) from Nagoya University under the direction of Professor Hisashi Yamamoto. He has been granted a Fellowship of the Japan Society for the Promotion of Sciences (JSPS) for Japanese Junior Scientists (1992-1995), during which he joined the group of Professor Julius Rebek, Jr. at MIT as a postdoctoral fellow (1994-1995). He was appointed as an assistant professor at Hokkaido University in 1995 and promoted to a lecturer (1998). He moved to Kyoto University as an associate professor (2001), and became a full professor of Nagoya University in 2006. He was awarded the Chugai Award in Synthetic Organic Chemistry, Japan (1997), the Japan Chemical Society Award for Young Chemist (1999), the Thieme Journal Award (2006), the JSPS Prize (2010), the IBM Japan Science Prize (2011) and the Inoue Prize for Science (2013). His current research interests are focused on the development of novel and useful synthetic methodologies based on the molecular design and precise structural control of chiral organic ion-pair catalysts.

Selected Publications

(1) “*In Situ* Generation of Ion-Paired Chiral Ligands: Rapid Identification of the Optimal Ligand for Palladium-Catalyzed Asymmetric Allylation”, K. Ohmatsu, Y. Hara, T. Ooi, *Chem. Sci.* **2014**, *5*, 3645-3650.

(2) “Ligand-Enabled Multiple Absolute Stereocontrol in Metal-Catalysed Cycloaddition for Construction of Contiguous All-Carbon Quaternary Stereocentres”, K. Ohmatsu, N. Imagawa, T. Ooi, *Nature Chem.* **2014**, *6*, 47-51.

(3) “Catalytic Asymmetric Oxidation of *N*-Sulfonyl Imines with Hydrogen Peroxide–Trichloroacetonitrile System”, D. Uraguchi, R. Tsutsumi, T. Ooi, *J. Am. Chem. Soc.* **2013**, *135*, 8161-8164.

(4) “Exploiting the Modularity of Ion-Paired Chiral Ligands for Palladium-Catalyzed Enantioselective Allylation of Benzofuran-2(3*H*)-ones”, K. Ohmatsu, M. Ito, T. Kunieda, T. Ooi, *J. Am. Chem. Soc.* **2013**, *135*, 590-593.

(5) “Highly Regio-, Diastereo-, and Enantioselective 1,6- and 1,8-Additions of Azlactones to Di- and Trienyl *N*-Acylpyrroles”, D. Uraguchi, K. Yoshioka, Y. Ueki, T. Ooi, *J. Am. Chem. Soc.* **2012**, *134*, 19370-19373.

(6) “Catalytic Asymmetric Ring Openings of Meso and Terminal Aziridines with Halides Mediated by Chiral 1,2,3-Triazolium Silicates”, K. Ohmatsu, Y. Hamajima, T. Ooi, *J. Am. Chem. Soc.* **2012**, *134*, 8794-8797.

(7) “Ionic Nucleophilic Catalysis of Chiral Ammonium Betaines for Highly Stereoselective Aldol Reaction from Oxindole-Derived Vinylic Carbonates”, D. Uraguchi, K. Koshimoto, T. Ooi, *J. Am. Chem. Soc.* **2012**, *134*, 6972-6975.

(8) “Ion-Paired Chiral Ligands for Asymmetric Palladium Catalysis”, K. Ohmatsu, M. Ito, T. Kunieda, T. Ooi, *Nature Chem.* **2012**, *4*, 473-477.

Ion-Pairing in Ligand Design for Asymmetric Palladium Catalysis

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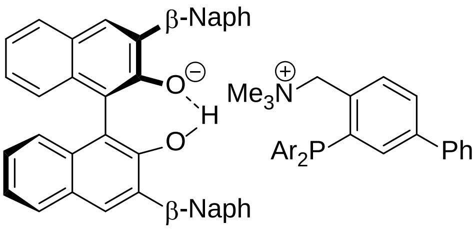
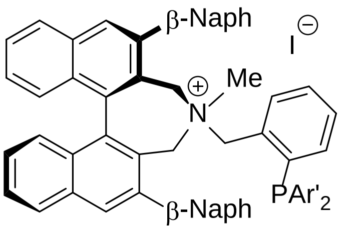
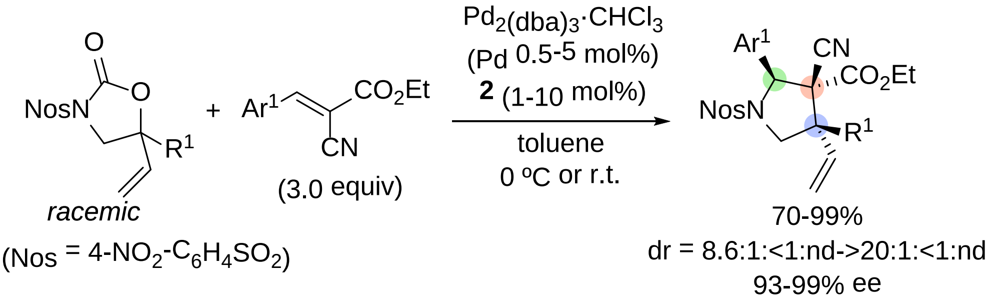
The design and preparation of chiral ligands is continuously a subject of central importance for developing transition-metal-catalyzed asymmetric transformations because the structural and electronic properties of the chiral ligand have a pivotal influence on the activity and stereocontrolling ability of the catalysts. However, challenge associated with this endeavor remains formidable in view of the complexity of ligand elaboration, synthesis, and optimization; that probably originates from the general notion of an effective ligand as a single chiral molecule equipped with coordinative functional groups. During the course of our research on the chiral organic ion-pair catalysis,[1,2] we were interested in addressing this issue and introduced a new strategy for the design of a chiral ligand for asymmetric transition-metal catalysis. Our approach was based on the development of an achiral ammonium-phosphine hybrid ligand paired with a chiral binaphtholate anion. This ion-paired chiral ligand **1** imparts a remarkable stereocontrolling ability to its palladium complex, thereby achieving a highly enantioselective allylic alkylation of α-nitrocarboxylates.[3] This approach showed vast potential in the development of transition-metal-catalyzed stereoselective bond-forming reactions.[4] Moreover, recent development of a new class of ion-paired chiral ligand **2** allowed us to solve very challenging synthetic problems such as asymmetric construction of contiguous all-carbon quaternary stereocenters.[5] In this lecture, the detail of this research stream will be presented.



1 (Ar = 4-Cl-C_6H_4)



2 (Ar' = 4-CF_3-C_6H_4)



1. D. Uraguchi, T. Ooi, *J. Synth. Org. Chem. Jpn.* **2010**, *68*, 1185-1194.
2. K. Ohmatsu, M. Kiyokawa, T. Ooi, *J. Am. Chem. Soc.* **2011**, *133*, 1307-1309.
3. K. Ohmatsu, M. Ito, T. Kunieda, T. Ooi, *Nature Chem.* **2012**, *4*, 473-477.
4. K. Ohmatsu, M. Ito, T. Kunieda, T. Ooi, *J. Am. Chem. Soc.* **2013**, *135*, 590-593.
5. K. Ohmatsu, N. Imagawa, T. Ooi, *Nature Chem.* **2014**, *6*, 47-51.

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Selected Publications

(1) Design, Synthesis, Spectral Investigations and Biological Activity of Fluorinated Phthalocyanine Conjugated with Galactose and Comparison to its Non-fluorinated Counterpart, Mori, N., Yoshiyama, H., Tokunaga, E., Iida, N., Hayashi, M., Obata, T., Tanaka, M. Shibata, N., *J. Fluorine Chem.* **2014**, doi:10.1016/j.jfluchem.2014.11.003.

(2) Pentafluorosulfanyl (SF_5) in dyes: C_3-Regioselective Synthesis of α-Mono-substituted Subphthalocyanine with SF_5-phenyl Group, Iida, N., Tokunaga, E., Saito, N., Shibata, N., *J. Fluorine Chem.* **2014**, doi.org/10.1016/j.jfluchem.2014.08.016.

(3) Synthesis and Property of Novel Phthalocyanine having a 3,5-Bis-pentafluorosulfanylphenyl Group on the α-Peripheral Position, Iida, N., Tokunaga, E., Saito, N., Shibata, N., *J. Fluorine Chem.* **2014**, 168, 93-98.

(4) Redox Chemistry of Trifluoromethyl Sulfonium Salts as CF_3 Radical Sources, Mizuta, S., Verhoog, S., Wang, X., Shibata, N., Gouverneur, V., Médebielle, M., *J. Fluorine Chem.* **2013**, 155, 124-131.

(5) Cinchona Alkaloid/TMAF Combination: Enantioselective Trifluoromethylation of Aryl Aldehydes, Kawai, H., Mizuta, S., Tokunaga, E., Shibata, N., *J. Fluorine Chem.* **2013**, 152, 46-50.

(6) *N*-2-Iodobenzylcinchoninium Bromide is Effective for Catalytic Enantioselective Trifluoromethylation of Azomethine Imines in Solkane® 365mfc, Okusu, S., Kawai, H. Xu, X-H., Tokunaga, E., Shibata, N., *J. Fluorine Chem.* **2012**, 143, 216-219.

(7) 3,5-Bis(pentafluorosulfanyl)phenylboronic Acid: A New Organocatalyst for Conia-ene Carbocyclization of 1,3-Dicarbonyl Compounds having Terminal Alkynes, Yang, Y.-D., Lu, X., Tokunaga, E., Shibata, N., *J. Fluorine Chem.* **2012**, 143, 204-209.

(8) Robust Synthesis of Trifluoromethionine and its Derivatives by Reductive Trifluoromethylation of Amino Acid Disulfides by $CF_3I/Na/Liq.NH_3$ System, Yasui, H., Yamamoto, T., Tokunaga, E., Shibata, N., *J. Fluorine Chem.* **2012**, 132, 186-189.

Novel Reagents for Electrophilic Pentafluorosulfanylphenylation of *C*, *O*, *S* and *N*-Nucleophiles

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Trifluoromethylated aromatic compounds have prestigious potions in the fields of medicinal chemistry, agrochemistry and material sciences, and the synthetic methodologies for the trifluoromethylated aromatic compounds are well-established in recent years. Pentafluorosulfanyl (SF_5)-substituted aromatic compounds (SF_5)Ar have now become nest targets as future materials in recent years due to their high lipophilicity and strong electron-withdrawing character. However, the direct introduction of SF_5 group into organic molecules needs gaseous toxic reagents (Br-SF_5, Cl-SF_5) and stepwise methods required for sulfur compounds and elemental fluorine with tedious procedure. Our group is interested in the development of novel methods for the synthesis of the SF_5-substituted aromatic compounds.[1] We disclose herein the novel electrophilic pentafluorosulfanylphenylation regents for the direct introduction of SF_5-containing aryl group for target compounds. Corresponding SF_5Ar-containing compounds were obtained in good to high yields under mild conditions. The application of this method will be discussed in the presentation.

1. Pentafluorosulfanyl (SF_5) in dyes: C_3-Regioselective Synthesis of α-Mono-substituted Subphthalocyanine with SF_5-phenyl Group, Iida, N., Tokunaga, E., Saito, N., Shibata, N., *J. Fluorine Chem.* **2014**, doi.org/10.1016/j.jfluchem.2014.08.016; Synthesis and Property of Novel Phthalocyanine having a 3,5-Bis-pentafluorosulfanylphenyl Group on the α-Peripheral Position, Iida, N., Tokunaga, E., Saito, N., Shibata, N., *J. Fluorine Chem.* **2014**, 168, 93-98; Bis(pentafluorosulfanyl)phenyl Azide as an Expeditious Tool for Click Chemistry toward Antitumor, Yang, Y., Tokunaga, E., Akiyama, H., Saito, N., Shibata, N., *ChemMedChem*, **2014**, 9, 913-917; 3,5-Bis(pentafluorosulfanyl)phenylboronic Acid: A New Organocatalyst for Conia-ene Carbocyclization of 1,3-Dicarbonyl Compounds having Terminal Alkynes, Yang, Y.-D., Lu, X., Tokunaga, E., Shibata, N., *J. Fluorine Chem.* **2012**, 143, 204-209.

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Selected Publications

(1) α-Fluoroalkylamines - a new source of unhydrated anion fluoride, I, Fluorotrimethylamine, Knunyanz I.L., Delyagina N.I., Igumnov S.M., *Russ Chem Bull.* **1981**, *#4*, 857-859.
(2) α-Fluoroalkylamines - a new source of unhydrated anion fluoride, II, α, α-Difluorotrimethylamine, Knunyanz I.L., Delyagina N.I., Igumnov S.M., *Rus Chem Bul.* **1981**, *#4*, 860-863.
(3) α-Fluoroalkylamines - a new source of unhydrated anion fluoride, III, ^{19}F NMR Spectra of perfluorocarboanions generated with aim of N, N, N', N'-tetramethylformamidinium bifluoride, Knunyanz I.L., Delyagina N.I., Igumnov S.M., *Rus Chem Bul.* **1981***, #10*, 2238-2243.
(4) α-Fluoroalkylamines - a new source of unhydrated anion fluoride, IV, acylation of perfluoroalkylcarboanions by carboxylic acid fluoroanhydrides NMR Spectra of perfluorocarboanions generated with aim of N, N, N', N'-tetramethylformamide, Knunyanz I.L., Delyagina N.I., Igumnov S.M., *Rus Chem Bul.* **1981**, *#10*, 2238-2243.
(5) α-Fluoroalkylamines - a new source of unhydrated anion fluoride, V, N, N -dimethylmethyleneimmonium perfluoroalcoxides and their reaction with perfluoroolefins, Knunyanz I.L., Delyagina N.I., Igumnov S.M.,Zeifman U.V., *Russ Chem Bull.* **1984**, *#4*, 827-832.
(6) α-Fluoroalkylamines - a new source of unhydrated anion fluoride, VI, Hexamethylguanidinium fluorideperfluoroolefins, VI, Knunyanz I.L., Delyagina N.I., Igumnov S.M., *Russ Chem Bull.* **1986**, *#6*, 1315-1317.
(7) Replacement of iodine in tertiary perfluoroalkyliodides to nucleophiles, Pletnev S.I., Igumnov S.M., *Russ Chem Bull.* **1988**, *#12*, 2877.
(8) Polar addition of perfluoroterthexcyliodide to alkenes and alkynes, Pletnev S.I. Rozhkov I.N., Rempel G.D., Ponomarev V.I., Deev L.E., Shaidurov V.S., Igumnov S.M., *Russ Chem Bull.* **1989**, *#9*, 2057-2061.
(9) Oxidative properties of perfluoroalkylhalogenides, Pletnev S.I. Rozhkov I.N., Rempel G.D., Deev L.E., Bekker G.Y., Igumnov S.M., *Russ Chem Bull.* **1989***, #10*, 2222-2224.

(10) The first sample of electrophilic addition of perfluoroalkyliodides to unsaturated compounds, Pletnev S.I. Rozhkov I.N., Igumnov S.M., *Russ Chem Bull.* **1990**, *#1*,

226-227.
(11) Reduction of CF_3-group in polyfluoroaromatic compounds, Merkulov K, Igumnova E.V, Nefedova R., Don V.L., Igumnov S.M., *Fluorine notes.* **2001**, *#6(19).*
(12) Copper salt-catalysed reaction of perfluoroalkyl halieds with olefins, Vyazkov V.A., Narinyan K.E, Igumnov S.M., *Mendeleev Commun.* **2006**,(3) 189-190
(13) Copper's perform in the synthesis of fluoroalkylsilanes at interaction of fluoroalkylhalogenides with silylation agent at the presence of zink-copper couple, Menshikov V.K., Boiko V., Tyutyunov A.A, Sterlin S.P., Igumnov S.M., Fluorine notes, **2012**, *#6*(85)
(14) Preparative method for higher fluoroalkylsilanes, Boiko V., Tyutyunov A.A, Don V.L., Igumnov S.M., Fluorine notes, **2013**, *#6*(91)
(15) Preparative method for polyfluoroaryltrimethylsilane, Boiko V., Tyutyunov A.A, Don V.L., Igumnov S.M., Fluorine notes, **2013**, *#6*(91)
(16) Production of pentafluorophenol by oxidation of trimethyl(pentafluorophenyl)silane, Boiko V., Tyutyunov A.A, Don V.L., Igumnov S.M., Fluorine notes, **2013**, *#6*(91)
(17) Unusual reaction of (trifluoromethyl)trimethylsilane with natrium borane, Boiko V., Tyutyunov A.A, Igumnov S.M., Fluorine notes, **2011**, *#1*(74)

α-Fluoroalkylamines - A New Source of Unhydrated Fluorine Anion

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It is shown that dialkylaminofluoromethanes are the sources of fluorine anion for perfluoroolefins and perfluorocarbonyl compounds and react with the formation of the introduction products of saturated compound under C-F bond or perfluorinated anions stabilized by ammonium cation. C-C bond of dialkylaminomethyl group with perfluoroalkyl residue is easily exposed to halogenolysis with tertiary perfluoroalkyl halides formation. It is shown that they add to alkenes at room and lower temperatures. There evaluated reduction potentials of primary, secondary and tertiary perfluoroalkyliodies, It is shown that tertiary perfluoroalkyliodides are stronger oxidizing agents or iodine. It is found "red-ox" system Cu^{2+}/N_2H_4 initiating addition of perfluoroalkyliodides to alkenes.

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Takashi Yamazaki is currently a Professor of Chemistry at Tokyo University of Agriculture and Technology and the head of this department. He was born in 1957 in Nagano, Japan and raised in Kawasaki. He received his PhD degree in 1986 from Tokyo Institute of Technology (TIT) under the supervision of the late Professor Nobuo Ishikawa as the last PhD student in this laboratory. He was appointed as an Assistant Professor at Tokyo Institute of Technology, and has been in this position from 1986-2002. During this period, he joined the Professor John T. Welch's laboratory at the State University of New York at Albany as a postdoctoral fellow in the season of 1988-1989. In 2002 after finishing the postdoc work and returned to TIT, he moved to Department of Applied Chemistry, Tokyo University of Agriculture and Technology as an associate professor and promoted to a full professor in 2009.

He received a couple of prizes like 1) the Tejima Research Award Encouraging Prize in 1987, 2) The Chemical Society Award of Japan for Young Chemists in 1992, 3) Tejima Research Award Nakamura Prize in 1993, and 4) Takeda International Contribution Award in 2007.

He has published about 160 papers including patents and book chapters. He is now a member of the Chemical Society of Japan, the American Chemical Society as well as its fluorine division, and the Society of Synthetic Organic Chemistry, Japan, and also has played a role as a secretary of treasurer of the Society of Fluorine Chemistry, Japan, and a member of the Editorial Boards of Journal of Fluorine Chemistry.

His main interests focus on 1) the stereoselective syntheses of fluorinated compounds starting from easily available starting materials, 2) the development of novel routes by employment of characteristics of fluorine atoms, 3) the clarification of fluorine's characteristics in synthetic chemistry from the computational point of view.

Selected Publications

(1) *Facile One-pot Preparation of Allylic Alcohols with a Fluorine-containing Alkyl Group at the γ-Position*, Yamazaki, T.; Ichikawa, M.; Kawasaki-Takasuka, T.; Yamada, S. *J. Fluorine Chem.* **2013**, *155*, 151–154.

(2) *Construction of Chiral Trifluoromethylated Materials by Combination of Stereochemically Predictable S_N2' Reaction and Ireland-Claisen Rearrangement*, Ichikawa, T.; Kawasaki-Takasuka, T.; Yamada, S.; Yamazaki, T.; Kubota, T. *J. Fluorine Chem.* **2013**, *152*, 38–45.

(3) *Stereodivergent Formation of Fluorine-containing Enamides*, Ota, S.; Kawasaki-Takasuka, T.; Yamazaki, T.; Kubota, T. *J. Fluorine Chem.* **2012**, *143*, 155–160.

(4) *Divergent Preparation of Allenyl Tosylates and -Tosyloxy Ketones by Facile and Efficient Isomerization of CF_3-Containing Propargylic Tosylates*, Watanabe, Y.; Yamazaki, T. *J. Fluorine Chem.* **2010**, *131*, 646–651.

(5) *Incorporation of Fluoroprolines to Proctolin: Study on the Effect of A Fluorine Atom toward Peptidic Conformation*, Kitamoto, T.; Ozawa, T.; Abe, M.; Marubayashi, S.; Yamazaki, T. *J. Fluorine Chem.* **2008**, *129*, 286–293.

(6) *The Effect of Fluoromethyl Groups on the Diastereoselectivity in the Electrophilic Alkylation*, Tamura, K.; Yamazaki, T.; Kitazume, T.; Kubota, T. *J. Fluorine Chem.* **2005**, *126*, 918–930.

Novel Transformations of 4,4,4-Trifluorobut-2-yn-1-ol Initiated by Abstraction of the Propargylic Protons

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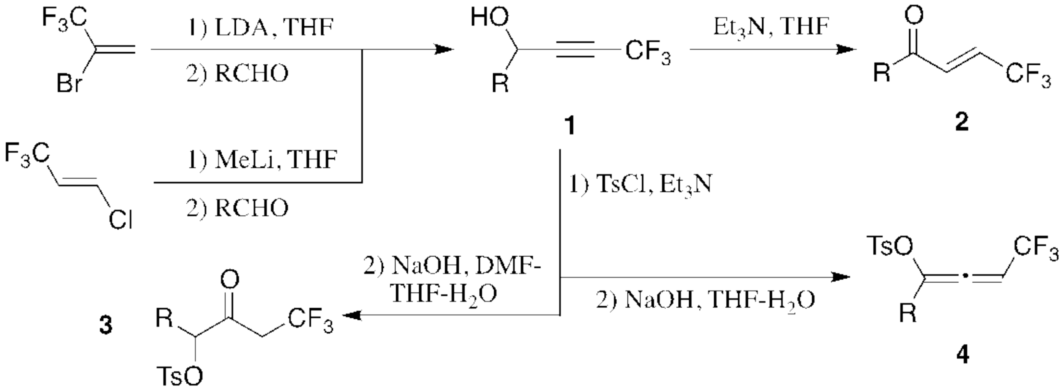
We have previously reported the development of the facile preparation methods of 4,4,4-trifluorobut-2-yn-1-ols from industrially easily available 2-bromo-3,3,3-trifluoro- propene [1] and 1-chloro-3,3,3-trifluoropropene [2], and propargylic alcohols **1** thus obtained have been employed for the syntheses of a wide variety of 6-deoxy-6,6,6-trifluoro sugars [1], allenes [3], heterocyclic compounds [4], and so on. During our research for further utilization of these alcohols **1**, we have by chance found out [5] the facile transformation of **1** to the corresponding α,β-unsaturated ketones **2** in excellent isolated yields with high level of *E* stereoselectivity. This redox-type reaction seemed to occur by the initial abstraction of the propargylic proton by triethylamine, followed by the re-protonation at the carbon atom possessing a CF_3 group and keto-enol tautomerization. Our computation unambiguously revealed the higher lability of this propargylic proton than the one in the OH moiety. This result allowed us to further study the related system and we successfully found out that subjection of **1** after tosylation to a NaOH solution in a mixed solvent system of THF and water with or without DMF affected the conversion to 1,1,1-trifluoro-4-tosyloxybutan-2-ones **3** or allenyl tosylates **4**, respectively, in good to excellent chemical yields.



References

[1] Yamazaki, T.; Mizutani, K.; Kitazume, T. *J. Org. Chem.* **1995**, *60*, 6046–6056.
[2] Miyagawa, A.; Naka, M.; Yamazaki, T.; Kawasaki-Takasuka, T. *Eur. J. Org. Chem.* **2009**, 4395–4399.
[3] a) Hanzawa, Y.; Kawagoe, K.; Yamada, A.; Kobayashi, Y. *Tetrahedron Lett.* **1985**, *26*, 219–222. b) Yamazaki, T.; Yamamoto, T.; Ichihara, R. *J. Org. Chem.* **2006**, *71*, 6251–6253.
[4] a) Qing, F.-L.; Gao, W.-Z.; Ying, J.-W. *J. Org. Chem.* **2000**, *65*, 2003–2006. b) Sibous, L.; Tipping, A. E. *J. Fluorine Chem.* **1993**, *62*, 39–49. c) Watanabe, Y.; Yamazaki, T. *Synlett* **2009**, 3352–3354. d) Zhang, C.-T.; Zhang, X.-G.; Qing, F.-L. *Tetrahedron Lett.* **2008**, *49*, 3927–3930.
[5] Yamazaki, T.; Kawasaki-Takasuka, T.; Furuta, A.; Sakamoto, S. *Tetrahedron* **2009**, *65*, 5945–5948.