

## 研究期間全年度 研究業績

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### 1. 発表論文等（査読付き論文，著書，総説等の発表状況）

- (1) Oxidative Arylation Mediated by Naphthalene-1,8-diylbis(diphenylmethylum): Synthetic Route to Triarylsulfonium Salts  
Tanabe, H.; Kawai, T.; Saitoh, T.; Ichikawa, J.\* *Chem. Lett.* **2010**, *39*, 56–57.
- (2) Transition-Metal-Catalyzed Electrophilic Activation of 1,1-Difluoro-1-alkenes: Oxindole Synthesis via Intramolecular Amination  
Tanabe, H.; Ichikawa, J.\* *Chem. Lett.* **2010**, *39*, 248–249.
- (3) Indium(III)-catalyzed Coupling between Alkynes and Aldehydes to  $\alpha,\beta$ -Unsaturated Ketones  
Miura, K. \*; Yamamoto, K.; Yamanobe, A.; Ito, K.; Kinoshita, H.; Ichikawa, J.; Hosomi, A. *Chem. Lett.* **2010**, *39*, 766–767.
- (4) Rapid and Slow Generation of 1-Trifluoromethylvinylolithium: Syntheses and Applications of  $\text{CF}_3$ -Containing Allylic Alcohols, Allylic Amines, and Vinyl Ketones  
Nadano, R.; Fuchibe, K.; Ikeda, M.; Takahashi, H.; Ichikawa, J.\* *Chem. Asian J.* **2010**, *5*, 1875–1883.
- (5) Synthetic Methods for Heterocycles and Carbocycles Bearing Fluorinated One-Carbon Units ( $=\text{CF}_2$ ,  $\text{CHF}_2$ , or  $\text{CF}_3$ ): Intramolecular Reaction of 2-Trifluoromethyl-1-alkenes  
Ichikawa, J.\* *J. Synth. Org. Chem., Jpn.* **2010**, *68*, 1175–1184.
- (6) A Facile Synthesis of 1,1-Difluoroallenes from Commercially Available 1,1,1-Trifluoro-2-iodoethane  
Oh, K.; Fuchibe, K.; Ichikawa, J.\* *Synthesis* **2011**, 881–886.
- (7) 5-endo-trig Cyclization of 1,1-Difluoro-1-Alkenes: Synthesis of 3-Butyl-2-Fluoro-1-Tosylindole(1*H*-Indole,3-Butyl-2-Fluoro-1-[(4-Methylphenyl) Sulfonyl]-)  
Ichikawa, J.\* *Org. Synth.* **2011**, *88*, 162–167.
- (8) Illusory Molecular Expression of “Penrose Stairs” by an Aromatic Hydrocarbon  
Nakanishi, W.; Matsuno, T.; Ichikawa, J.; Isobe, H.\* *Angew. Chem. Int. Ed.* **2011**, *50*, 6048–6051.
- (9) Domino Friedel–Crafts-Type Cyclizations of Difluoroalkenes Utilizing the  $\alpha$ -Cation-Stabilizing Effect of Fluorine: An Efficient Method for Synthesizing Angular PAHs

- Fuchibe, K.; Jyono, H.; Fujiwara, M.; Kudo, T.; Yokota, M.; Ichikawa, J.\* *Chem. Eur. J.* **2011**, *17*, 12175–12185.
- (10) Facile Synthesis of  $\beta,\beta$ -Difluorostyrenes via the Negishi Coupling of Thermally Stable 2,2-Difluorovinyl Zinc-TMEDA Complex  
Fujita, T.; Ichitsuka, T.; Fuchibe, K.; Ichikawa, J.\* *Chem. Lett.* **2011**, *40*, 986–988.
- (11) NHC-Catalyzed Difluorocarbene Generation and Its Application to Aryl Difluoromethyl Ether Synthesis  
Fuchibe, K.; Koseki, Y.; Sasagawa, H.; Ichikawa, J.\* *Chem. Lett.* **2011**, *40*, 1189–1191.
- (12) NHC-Catalyzed Generation of Difluorocarbene and its Application to Difluoromethylation of Oxygen Nucleophiles  
Fuchibe, K.; Koseki, Y.; Aono, T.; Sasagawa, H.; Ichikawa, J.\* *J. Fluorine Chem.* **2012**, *133*, 52–60.
- (13) Facile Synthesis of Substituted 1,1-Difluoroallenes via C=O Difluorovinylideneation  
Oh, K.; Fuchibe, K.; Yokota, M.; Ichikawa, J.\* *Synthesis*, **2012**, *44*, 857–861.
- (14) 1,1-Difluoro-1-alkenes as New Electrolyte Additives for Lithium Ion Batteries  
Kubota, T. \*; Ihara, M.; Katayama, S.; Nakai, H.; Ichikawa, J. *J. Power Sources*, **2012**, *207*, 141–149.
- (15)  $\gamma$ -Selective Addition to 1,1-Difluoroallenes: Three-Component Coupling Leading to 2,2-Disubstituted 1,1-Difluoroalkenes  
Fuchibe, K.; Ueda, M.; Yokota, M.; Ichikawa, J.\* *Chem. Lett.* **2012**, *41*, 1619–1621.
- (16) Substitutions of Two Fluorine Atoms in a Trifluoromethyl Group: Regioselective Synthesis of 3-Fluoropyrazoles  
Fuchibe, K.; Takahashi, M.; Ichikawa, J.\* *Angew. Chem. Int. Ed.* **2012**, *51*, 12059–12062.
- (17) Nucleophilic 5-*endo-trig* Cyclization of 3,3-Difluoroallylic Ketone Enolates: Synthesis of 5-Fluorinated 2-Alkylidene-2,3-dihydrofurans  
Fujita, T.; Sakoda, K.; Ikeda, M.; Hattori, M.; Ichikawa, J.\* *Synlett* **2013**, *24*, 57–60.
- (18) Redox switching of conjugation length using 9,9,10,10-tetraaryl-9,10-dihydrophenanthrene as an ON/OFF unit: Preparation, X-ray structure, and redox properties of perfluorobiphenyl derivative and its  $S_NAr$  reactions to  $\pi$ -extended analogues  
Suzuki, T. \*; Tamaoki, H.; Katoono, R.; Fujiwara, K.; Ichikawa, J.; Fukushima, T. *Chem. Lett.* **2013**, *42*, 703–705.
- (19) Domino Synthesis of Fluorine-Substituted PAHs: 1,1-Difluoroallenes as Synthetic Platforms  
Fuchibe, K.; Mayumi, Y.; Zhao, N.; Watanabe, S.; Yokota, M.; Ichikawa, J.\* *Angew. Chem. Int. Ed.* **2013**, *52*, 7825–7828.

- (20) Facile Synthesis of Unsymmetrical 1,1-Diaryl-2,2-difluoroethenes via Stepwise Coupling of 1,1-Dibromo-2,2-difluoroethenes  
Fujita, T. Suzuki, N.; Ichitsuka, T.; Ichikawa, J.\* *J. Fluorine. Chem.* **2013**, *155*, 97–101.
- (21) A New Organic Two-Electron Oxidant: 9,10-Diaryl-9,10-dihydroanthracene-9,10-bis(ylum)  
Ichikawa, J.\*; Tanabe, H.; Yoshida, S.; Kawai, T.; Shinjo, M.; Fujita, T. *Chem. Asian J.* **2013**, *8*, 2588–2591.
- (22) Nucleophilic Addition of  $\alpha$ -(Dimethylsilyl)nitriles to Aldehydes and Ketones  
Jinzaki, T.; Arakawa, M.; Kinoshita, H.; Ichikawa, J.; Miura, K. \* *Org. Lett.* **2013**, *15*, 3750–3753.
- (23) Two-Step Synthesis of Difluoromethyl-Substituted 2,3-Dihydrobenzoheteroles  
Fujita, T.; Sanada, S.; Chiba, Y.; Sugiyama, K.; Ichikawa, J.\* *Org. Lett.* **2014**, *in press* (DOI: 10.1021/ol5001582) .
- (24) Nucleophilic 5-endo-trig Cyclization of 3,3-Difluoroallylic Metal Enolates and Enamides: Facile Synthesis of Ring-Fluorinated Dihydroheteroles  
Fujita, T.; Ikeda, M.; Hattori, M.; Sakoda, K.; Ichikawa, J.\* *Synthesis* **2014**, *in press* (DOI: 10.1055/s-0032-1317709).
- (25) Double C-F Bond Activation via  $\beta$ -Fluorine Elimination: Nickel-Mediated [3+2] Cycloaddition of 2-Trifluoromethyl-1-alkenes with Alkynes  
Ichitsuka, T.; Fujita, T.; Arita, T.; Ichikawa, J.\* *Angew. Chem. Int. Ed.* **2014**, *in press*.

## 2 . 学会発表等（国内外の招待講演および国際会議での発表状況）

- (1) Friedel–Crafts Cyclizations of Fluoro Alkenes Directed toward Polycyclic Aromatic Hydrocarbon (PAH) Synthesis  
Ichikawa, J. 3rd Korea–Japan–China Joint Seminar on Fluorine Chemistry, Daejeon, 2010, 9, 9 (招待講演) .
- (2) New Entry to Fluorinated PAHs: Palladium(II)-Catalyzed Electrophilic Cyclization of 1,1-Difluoro-1-alkenes  
Ichikawa, J. 6th International Symposium on Integrated Synthesis (ISIS-6), Kobe, 2010, 10, 23 (口頭発表) .
- (3) Transformation of C–F Bonds via Electrophilic Activation of Fluoro Alkenes and its Application to PAH Synthesis  
Ichikawa, J. Yonsei University, Wonju, Korea, 2010, 11, 11 (招待講演) .
- (4) 5-endo Cyclizations Promoted by Fluorine Substituent and their Application to Fluoroheterocycle Synthesis

- Ichikawa, J. Korea Research Institute of Chemical Technology, Daejeon, Korea, 2010, 11, 12 (招待講演) .
- (5) Transformation of C–F bonds via electrophilic activation of fluoro alkenes  
Ichikawa, J. Pacifichem 2010, Honolulu, Hawaii, 2010, 12, 15 (招待講演) .
- (6) Indium(III)-Catalyzed Cyclization of 1,1-Difluoroallenes: Construction of Naphthalene and Phenanthrene Frameworks  
Fuchibe, K.; Mayumi, Y.; Wang, K.; Yokota, M.; Ichikawa, J. Pacifichem 2010, Honolulu, Hawaii, 2010, 12, 17 (ポスター発表) .
- (7) Cationic palladium(II)-catalyzed Friedel-Crafts-typecyclizations of 1,1-difluoro-1-alkenes  
Fuchibe, K.; Morikawa, T.; Ichitsuka, T.; Fujita, D.; Tanabe, H. ; Yokota, M. ; Ichikawa, J. Pacifichem 2010, Honolulu, Hawaii, 2010, 12, 16 (ポスター発表) .
- (8) フルオロアルケンの求電子的活性化と環化反応 --含フッ素ヘテロ環化合物から多環式芳香族炭化水素まで --  
市川淳土, 第1回大塚有機合成シンポジウム, 徳島, 2011.8.22 (招待講演) .
- (9) In(III)-Catalyzed Synthesis of F-PAHs: Domino Cyclization- Ring Expansion Reactions of 1,1-Difluoroallenes  
Fuchibe, K.; Zhao, N.; Mayumi, Y.; Ichikawa, J. OMCOS-16, Shanghai, 2011.7.24–28 (ポスター発表) .
- (10) Electrophilic Cyclization of Fluoro Alkenes Directed toward PAH Synthesis  
Ichikawa, J., NTU-JSPS Joint Symposium, Singapore, 2011.8.2 (招待講演) .
- (11) Electrophilic Cyclization of Fluoro Alkenes Directed toward PAH Synthesis  
Ichikawa, J. 242nd ACS National Meeting, Denver, 2011.8.28 (招待講演) .
- (12) Synthesis of F-PAHs by In(III)-Catalyzed Domino Cyclization-Ring Expansion of 1,1-Difluoroallenes  
Fuchibe, K.; Zhao, N.; Mayumi, Y.; Ichikawa, J. ISIS-7, Kobe, 2011.10.10 (ポスター発表) .
- (13) Metal-Catalyzed Domino Difluorocyclopropanation-Ring Expansion of 2-Siloxy-1,3-dienes: Synthesis of Fluorinated Cyclic Silyl Enol Ethers  
Aono, T.; Sasagawa, H.; Fuchibe, K.; Ichikawa, J. ISOR-10, Yokohama, 2011.11. 21-24 (ポスター発表) .
- (14) Sequential Substitutions of 2-Trifluoromethyl-1-alkenes: Regioselective Synthesis of 3-Fluoropyrazoles  
Takahashi, M.; Hattori, M.; Fuchibe, K.; Ichikawa, J. ISOR-10, Yokohama, 2011.11. 21-24 (ポスター発表) .

- (15) *gem*-ジフルオロアルケンの求電子的活性化による多環式芳香族炭化水素の触媒的合成  
 淵辺耕平, 森川稔之, 上田 龍, 市川淳士, ICHAC-10 Pre-symposium in Tsukuba, つくば, 2012年5月19日(招待講演)。
- (16) Difluoroallene Chemistry: Preparation and Application  
 Ichikawa, J., 3rd International Symposium on Organofluorine Compounds in Biomedical, Materials and Agricultural Sciences, Valencia, 2012, 5, 21 (招待講演)。
- (17) フルオロアルケンの求電子的活性化と環構築  
 市川淳士, 平成24年度前期(春季)有機合成化学講習会, 東京, 2012年6月20日(招待講演)。
- (18) Regioselectivity-switchable allylic substitution of 3-bromo-3,3-difluoropropene with heteronucleophiles toward syntheses of fluorinated dihydrobenzoheteroles  
 Sugiyama, K.; Sanada, S.; Chiba, Y.; Fujita, T.; Ichikawa, J. 20th International Symposium on Fluorine Chemistry, Kyoto, 2012, 7, 24 (ポスター発表)。
- (19) Synthesis of substituted F-PAHs: Palladium(II)-catalyzed Friedel–Crafts-type cyclizations of 1,1-difluoro-1-alkenes via their electrophilic activation  
 Ueda, R.; Morikawa, T.; Tanabe, H.; Fuchibe, K.; Ichikawa, J. 20th International Symposium on Fluorine Chemistry, Kyoto, 2012, 7, 24 (ポスター発表)。
- (20) Synthesis of fluorinated PAHs by one-pot reactions of difluoroallenes  
 Fuchibe, K.; Zhao, N.; Ichikawa, J. 20th International Symposium on Fluorine Chemistry, Kyoto, 2012, 7, 26 (口頭発表)。
- (21) NHC-Catalyzed Generation of Difluorocarbene: Syntheses of Aryl Difluoromethyl Ethers and Difluoromethyl Imidates  
 Fuchibe, K.; Koseki, Y.; Aono, T.; Ichikawa, J. 4th Asian Silicon Symposium, Tsukuba, 2012, 10, 22 (ポスター発表)。
- (22) Facile Synthesis of Fluorinated Benzoheterole Derivatibes via Regioselective Allylic Substituion of 3-Bromo-3,3-difluoropropene  
 Sugiyama, K.; Sanada, S.; Chiba, Y.; Fujita, T.; Ichikawa, J. IKCOC-12, Kyoto, 2012, 11, 14 (ポスター発表)。
- (23) Electrophilic Activation and Cyclization of Fluoro Alkenes Directed toward PAH Synthesis  
 Ichikawa, J. Dasan Conference 2012: Green Chemical Industry for Enviroment and Health: Fluorine Conpounds, Changwon, Korea, 2012, 11, 15 (招待講演)。
- (24) Construction of fluorinated heterocycles: Intramolecular substitution of vinylic and allylic fluorines

Ichikawa, J. 245th ACS National Meeting & Exposition, New Orleans, 2013, 4, 8 (招待講演).

(25) ピンポイントフッ素化した多環式芳香族炭化水素 (F-PAH)

市川淳士, 物質・デバイス領域共同研究拠点 物質機能科学領域部会 第1回研究集会, 東京, 2013年6月26日 (招待講演).

(26) フッ素置換基の  $\alpha$ -カチオン安定化効果を利用する合成反応

市川淳士, 第48回有機反応若手の会, 守谷市, 2013年7月29日 (招待講演).

(27) Nickel-Catalyzed Fluoroarene Synthesis : [2+2+2] Cycloaddition of Difluoroethylene and Alkynes

Watabe, Y.; Ichitsuka, T.; Fujita, T.; Ichikawa, J. ISCC-10, Kyoto, 2013, 9, 25 (ポスター発表).

(28) Difluoroallene Chemistry: Preparation and Application

Ichikawa, J.; Fuchibe, K.; Mayumi, Y.; Zhao, N.; Yokota, M.; Oh, K.; Watanabe, S. 11th International Symposium on Organic Reaction, Taipei, 2013, 11, 20 (招待講演).

(29) 炭素 - フッ素結合を活用する環構築法

市川淳士, 2013ハロゲン利用ミニシンポジウム (第6回臭素化学懇話会年会), 松山, 2013年11月29日 (招待講演).

### 3. 特許

(1) 含フッ素化合物および該含フッ素化合物を用いた有機薄膜トランジスタ

旭硝子株式会社; 市川淳士, 山本今日子,  
特願 2013-007148 (2013. 1.18).

### 4. 学会・シンポジウム等の開催状況

(1) 向山アルドール反応40周年記念シンポジウム, ハイアットリージェンシー東京, 2013.8.31 (市川淳士, 実行委員)

(2) 第36回フッ素化学討論会, つくば国際会議場, 2013.10.3-4 (市川淳士, 実行委員長).

### 5. 受賞等

(1) 渡邊駿平 (修士2年)

優秀ポスター賞 有機反応若手の会, 2013.7.31

(2) 市塚知宏 (博士2年)

学生講演賞 日本化学会第93春季年会, 2013.4.18

- (3) 藤田健志 (助教)  
研究企画賞 (セントラル硝子) 2011 年度有機合成化学協会, 2011.12.6
- (4) 高橋正樹 (修士 2 年)  
最優秀ポスター賞 10th International Symposium on Organic Reactions, 2011.11.24
- (5) 趙男 (修士 2 年)  
優秀ポスター賞 第 22 回基礎有機化学討論会, 2011.9.22
- (6) 森川稔之 (修士 2 年)  
優秀ポスター賞 日本化学会第 4 回関東支部大会, 2010.9.21
- (7) 小関雄太 (修士 1 年)  
優秀ポスター賞 日本化学会第 4 回関東支部大会, 2010.9.21

## 6 . 新聞報道等

- (1) Molecular Visual Illusion, Chemistry Views, 2011.6  
([http://www.chemistryviews.org/details/ezone/1077237/Molecular\\_Visual\\_Illusion.html](http://www.chemistryviews.org/details/ezone/1077237/Molecular_Visual_Illusion.html))
- (2) 芳香環を使った分子のだまし絵 シクロビス [4] ヘリセンの合成  
深澤愛子(紹介記事執筆者), 月刊化学, 2012.1

## 7 . 国民との科学・技術対話

該当なし

## 8 . 領域内の共同研究の準備・実施状況とその成果

- (1) 共同研究先: 京都大学, 吉田潤一研究室 (領域代表)  
派遣人員 (派遣): 市塚知宏 (博士 2 年)  
派遣期間 (派遣): 2012.10.14 - 2012.10.27  
共同研究内容: マイクロリアクターを用いた含フッ素カルバニオンの発生と反応  
共同研究成果: 学会発表
- (2) 共同研究先: 北海道大学, 鈴木孝紀研究室 (A03 班, 計画班員)  
共同研究内容:  $^{19}\text{F}$ -NMR の測定と解析  
共同研究成果: 論文発表 [ 1.発表論文 (18) ]