

## 平成24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) Facile Synthesis of Substituted 1,1-Difluoroallenes via C=O Difluorovinylideneation  
Oh, K.; Fuchibe, K.; Yokota, M.; Ichikawa, J.\* *Synthesis*, **2012**, *44*, 857–861.
- (2) 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.
- (3)  $\gamma$ -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.
- (4) Substitutions of Two Fluorines in a trifluoromethyl Group: Regioselective Synthesis of 3-Fluoropyrazoles  
Fuchibe, K.; Takahashi, M.; Ichikawa, J.\* *Angew. Chem. Int. Ed.* **2012**, *51*, 12059–12062.
- (5) 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.
- (6) 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.*, 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) Catalytic Synthesis of Polycyclic Aromatic Hydrocarbons by Electrophilic Activation of *gem*-Difluoroalkenes  
Fuchibe, K.; Morikawa, T.; Ueda, R.; Ichikawa, J. ICHAC-10 Pre-symposium in Tsukuba, Tsukuba, Japan, 2012. 5. 19（招待講演）.
- (2) Difluoroallene Chemistry: Preparation and Application  
Ichikawa, J. 3rd International Symposium on Organofluorine Compounds in Biomedical, Materials and Agricultural Sciences, Valencia, Spain, 2012.5.19（招待講演）.

- (3) 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).
- (4) Construction of Fluorinated Heterocycles: Intramolecular Substitution of Vinylic and Allylic Fluorines  
Ichikawa, J. 8th Japanese-French Joint Seminar on Fluorine Chemistry, Kyoto, 2012.6.21 (招待講演).
- (5) 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 (口頭発表).
- (6) 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 (口頭発表).
- (7) Synthesis of fluorinated PAHs by one-pot reactions of difluoroallenes  
Fuchibe, K.; Zhao, N.; Ichikawa, J. 20th International Symposium on Fluorine Chemistry, Kyoto, 2012.7.24 (口頭発表).
- (8) 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).
- (9) Electrophilic Activation and Cyclization of Fluoro Alkenes Directed toward PAH Synthesis  
Ichikawa, J. Dasan Conference 2012: Green Chemical Industry for Environment and Health: Fluorine Compounds, Changwon, Korea, 2012.11.15 (招待講演).
- (10) Synthesis of Fluorinated Large PAHs via Tandem Ring Construction of Bis(difluoroallene)s  
Aihara, H.; Zhao, N.; Fuchibe, K.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表).
- (11) Development of New Carbon Source for Metal Difluorocarbene Complexes  
Bando, M.; Fuchibe, K.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表).

- (12) Nickel-Catalyzed Synthesis of 1,1-Difluoro-1,4-dienes via C–F bond Activation of a Trifluoromethyl Group  
Ichitsuka, T.; Fujita, T.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (13) A Study for Enantioselective Synthesis of Fluorohelicenes by a Friedel–Crafts-Type Cyclization of Difluoroalkenes  
Nakamura, S.; Fuchibe, K.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (14) Silver-Catalyzed Cyclization of  $\beta,\beta$ -Difluorostyrenes with an *o*-Nitrogen Substituent: Synthesis of 2-Fluoroindoles  
Nojima, T.; Yamashita, S.; Fujita, T.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (15) Regioselective Difluoroallylation with 3-Bromo-3,3-difluoropropene: Facile Synthesis of Fluorinated Benzoheterole Derivatives  
Sugiyama, K.; Sanada, S.; Chiba, Y.; Fujita, T.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (16) Two-Step Synthesis of PAHs via Brønsted Acid-Mediated Domino Cyclization of 1,1-Difluoro-1-alkenes  
Suzuki, N.; Fujita, T.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (17) A Facile Synthesis of Phenacenes via Intramolecular Dehydrative Cycloaromatization of (Biaryl-2-yl)acetaldehydes  
Takahashi, I.; Fujita, T.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (18) Rate-Tunable Generation of Difluorocarbene by Organocatalysts  
Takayama, R.; Aono, T.; Koseki, Y.; Fuchibe, K.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (19) Practical Synthesis of Substituted Fluorophenanthrenes via Indium-Catalysed Domino Reaction of 1,1-Difluoroallenes  
Watanabe, S.; Zhao, N.; Fuchibe, K.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .
- (20) Synthesis of Acenes by Domino Cationic Cyclization of Trifluoromethylalkenes  
Kitagawa, T.; Miura, K.; Fuchibe, K.; Ichikawa, J. 3rd International Symposium on Creation of Functional Materials, Tsukuba, 2012.12.10 (ポスター発表) .

### 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

該当なし

### 5. 受賞等

該当なし

### 6. 新聞報道等

該当なし

### 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，吉田研究室（A01 班，計画班員）

派遣人員（派遣）：市塚知宏（博士1年）1名

派遣期間（派遣）：2012.10.15-2012.10.26

共同研究内容： $\alpha$ -トリフルオロメチルビニルリチウムの発生と、求電子剤である $\alpha$ -ハロケトンとの反応をマイクロリアクターにより検討し、トリフルオロメチルアリルケトンの合成を行った。

共同研究成果：論文準備中

### (2) 共同研究先：北海道大学，鈴木研究室（A03 班，計画班員）

派遣人員（派遣）：なし

共同研究内容：フッ素芳香環を分子内に含むジカチオン種の発生とそのエレクトロクロミズム特性開発について、カチオン発生条件やフッ素化合物のスペクトル特性について、鈴木教授と研究打ち合わせならびに共同研究実験(サンプル送付による)を実施した。

共同研究成果：論文発表 "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 SNAr reactions to  $\pi$ -extended analogues"

Suzuki, T.\*; Tamaoki, H.; Katoono, R. ; Fujiwara, K.; Ichikawa, J.; Fukushima, T., *Chem. Lett.*, in press.