

平成22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) Catalyst-free and Catalytic Friedel-Crafts Alkylations of Indoles in SolkaneR 365mfc, an Environmentally Benign Alternative Solvent
Xu, X.; Kusuda, A.; Tokunaga, E.; Shibata, N.* *Green Chem.*, **2011**, *13*, 46-50.
- (2) Asymmetric Synthesis of Both Mirror Images of 3-Fluorothalidomide by Enantiodivergent Fluorination Using a Single, Cinchona Alkaloid
Yamamoto, T.; Suzuki, Y.; Ito, E.; Tokunaga, E.; Shibata, N.* *Org. Lett.* **2011**, *13*, 470-473.
- (3) Inherent Oxygen Preference in Enolate Monofluoromethylation and a Synthetic Entry to Monofluoromethyl Ethers
Nomura, Y.; Tokunaga, E.; Shibata, N.* *Angew. Chem. Int. Ed.*, **2011**, *50*, 1885–1889.
- (4) Cinchona Alkaloid-Catalyzed Asymmetric Trifluoromethylation of Alkynyl Ketones with Trimethylsilyl Trifluoromethane
Kawai, H.; Tachi, K.; Tokunaga, E.; Shiro, M.; Shibata, N.* *Org. Lett.* **2010**, *12*, 5104-5107.
- (5) Expedient Synthesis of Trifluoromethylated Heterocycles: Noncatalytic 1, 3-Dipolar Cyclization of Azomethine Imines with (α -Trifluoromethyl)acrylates
Ogawa, S.; Nishimine, T.; Tokunaga, E.; Shibata, N.* *Synthesis* **2010**, 3274-3281.
- (6) Enantioselective Synthesis of Trifluoromethyl-Substituted 2-Isoxazolines: Asymmetric Hydroxylamine/Enone Cascade Reaction
Matoba, K.; Kawai, H.; Furukawa, T.; Kusuda, A.; Tokunaga, E.; Nakamura, S.; Shiro, M.; Shibata, N.* *Angew. Chem. Int. Ed.*, **2010**, *49*, 5762-5766.
- (7) Trifluoroethoxy-Coating Improves the Axial Ligand Substitution of Subphthalocyanine
Shibata, N.*; Das, B.; Tokunaga, E.; Shiro, M.; Kobayashi, N.* *Chem. Eur. J.* **2010**, *16*, 7554-7562.
- (8) Cinchona Alkaloid/TiIV-Catalyzed Enantioselective Enamine-Trifluoropyruvate Condensation-Cyclization Reaction and Its Application to Drug-like Heterocycles
Ogawa, S.; Iida, N.; Tokunaga, E.; Shiro, M.; Shibata, N.* *Chem. Eur. J.* **2010**, *16*, 7090-7095.

- (9) Perfluoroisopropyl Zinc Phthalocyanines Conjugated with Deoxyribonucleosides: Synthesis, Photophysical Properties and In Vitro Photodynamic Activities
Das, B.; Tokunaga, E.; Tanaka, M.; Sasaki, T.; Shibata, N.* *Eur. J. Org. Chem.* **2010**, 2878-2884.
- (10) Synthesis of Benzene-centered Trinuclear Phthalocyanines by Triple-click Chemistry
Das, B.; Umeda, M.; Tokunaga, E.; Toru, T.; Shibata, N.* *Chem. Lett.* **2010**, 39, 337-338.
- (11) Enantioselective Friedel-Crafts Reaction of β -Trifluoromethylated Acrylates with Pyrroles and Its Application to the Synthesis of Trifluorinated Heliotridane
Huang, Y.; Tokunaga, E.; Suzuki, S.; Shiro, M.; Shibata, N.* *Org. Lett.* **2010**, 12, 1136-1138.
- (12) 2-Fluoro-1, 3-benzodithiole-1, 1, 3, 3-tetraoxide: A Reagent for Nucleophilic Monofluoromethylation of Aldehydes
Furukawa, F.; Goto, Y.; Kawazoe, J.; Tokunaga, E.; Nakamura, N.; Yang, Y.; Du, H.; Kakehi, A.; Shiro, M.; Shibata, N.* *Angew. Chem. Int. Ed.*, **2010**, 49, 1642-1647.
- (13) Solubility of Trifluoroethoxyphthalocyanines and -Subphthalocyanines in Liquid and Supercritical Carbon Dioxide
Das, B.; Tokunaga, E.; Shibata, N.*; Kobayashi, N.* *J. Fluorine Chem.* **2010**, 131, 652-654.
- (14) Self-disproportionation of Enantiomers of Heterocyclic Compounds Having a Tertiary Trifluoromethyl Alcohol Center on Chromatography with a Non-chiral System
Ogawa, S.; Nishimine, T.; Tokunaga, E.; Nakamura, S.; Shibata, N.* *J. Fluorine Chem.* **2010**, 131, 521-524.
- (15) Efficient Access to Extended Yagupolskii-Umemoto-Type Reagents: Triflic Acid Catalyzed Intramolecular Cyclization of ortho-Ethynylaryltrifluoromethylsulfanes
Matsnev, A.; Noritake, S.; Nomura, Y.; Tokunaga, E.; Nakamura, S.; Shibata, N.* *Angew. Chem. Int. Ed.*, **2010**, 49, 572-576.
- (16) Synthesis and Configurational Stability of (*S*)- and (*R*)-Deuteriothalidomides
Yamamoto, T.; Tokunaga, E.; Nakamura, S.; Shibata, N.; Toru, T. *Chem. Pharm. Bull.* **2010**, 58, 110-112.
- (17) Part1 C-C 結合生成反応, Part2 不斉 C-C 結合生成反応, Part3 C-X 結合生成反応
柴田哲男 In 使える！有機合成反応 241 実践ガイド; 丸岡啓二, 野崎京子, 石井康敬, 大寺純蔵, 富岡 清, Eds.; 化学同人, 2010; 1.10, 2.118,148, 3.158,159, pp 20,21, 238,239, 300,301, 320-323.
- (18) 求電子的トリフルオロメチル化試薬の創製と新展開
柴田哲男*, 則竹 瞬, 化学工業, **2010**, 61, 265-281.

(19)有機フッ素化学基礎—不斉合成

柴田哲男 In フッ素化学入門 2010 基礎と応用の最前線; 独立行政法人 日本
学術振興会; フッ素化学第 155 委員会, Eds; 三共出版, 2010; 2.2.3, pp 135-191.

(20)ドラッグライクな有機分子創出を目指した含フッ素複素環化合物の不斉合成

柴田哲男*, 小川真一, 月刊ファインケミカル, **2010**, *40*, 7-15

(21)Oxidation | C-X bond formation: C-X bond formation (X = halogen, S, Se)

Shibata, N, Xu, X-H; Suzuki S.; Cahard, D. -In *Comprehensive Chirality*; Geraghty, F, Edt.;
ELSEVIER, 2010; 6.11, 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) Self-disproportion of Enantiomers of Thalidomide on chromatography with a non-chiral system

Maeno, M.; Ito, E.; Yamamoto, T.; tokunaga, E.; Shibata, N. GLOBAL COE-RCMS International Symposium on Organic Chemistry and 7th Yoshimasa Hirata Memorial Lecture, Aichi, Japan, 2010.3.17 (ポスター発表).

(2) Catalytic Enantioselective Trifluoromethylation of Alkynyl Ketones and Synthesis of Aryl Heteroaryl Trifluoromethyl Carbinols

Kawai, H.; Tachi, K.; Tokunaga, E.; Shibata, N. GLOBAL COE-RCMS International Symposium on Organic Chemistry and 7th Yoshimasa Hirata Memorial Lecture, Aichi, Japan, 2010.3.17 (ポスター発表).

(3) Asymmetric Allylic Fluoroalkylation using FBSM

Furukawa, T.; Kawazoe, J.; Zhang, W.; Nishimine, T.; Tokunaga, E.; Shibata, N. GLOBAL COE-RCMS International Symposium on Organic Chemistry and 7th Yoshimasa Hirata Memorial Lecture, Aichi, Japan, 2010.3.17 (ポスター発表).

(4) Design and synthesis of novel electrophilic bromodifluoromethylating reagents

Mori, S.; Ryu, G.; Tokunaga, E.; Shibata, N. GLOBAL COE-RCMS International Symposium on Organic Chemistry and 7th Yoshimasa Hirata Memorial Lecture, Aichi, Japan, 2010.3.17 (ポスター発表).

(5) Catalytic Asymmetric Synthesis of Efavirenz, an HIV-1 Reverse Transcriptase Inhibitor

Kitayama, T.; Kawai, H.; Tokunaga, E.; Shibata, N. GLOBAL COE-RCMS International Symposium on Organic Chemistry and 7th Yoshimasa Hirata Memorial Lecture, Aichi, Japan, 2010.3.17 (ポスター発表).

- (6) Chiral Lewis Acid Catalysts for Enantioselective Reaction of β -Trifluoromethylated Acrylates with Pyrroles
Suzuki, S.; Huang, Y.; Tokunaga, E.; Shibata, N. GLOBAL COE-RCMS International Symposium on Organic Chemistry and 7th Yoshimasa Hirata Memorial Lecture, Aichi, Japan, 2010.3.17 (ポスター発表).
- (7) Expedient Synthesis of Trifluoromethylated Heterocycles by Noncatalytic 1,3-Dipolar Cyclization
Nishimine, T.; Ogawa, S.; Tokunaga, E.; Shibata, N. GLOBAL COE-RCMS International Symposium on Organic Chemistry and 7th Yoshimasa Hirata Memorial Lecture, Aichi, Japan, 2010.3.17 (ポスター発表).
- (8) Environmentally benign organic synthesis based on fluorine chemistry
Shibata, N. 23rd International Conference on ORGANIC PROCESS RESEARCH & DEVELOPMENT, Florida, USA, 2010.2.28-3.2 (招待講演).
- (9) Recent progress of monofluoromethylation reactions using FBSM and FBDT as synthetic equivalents for monofluoromethyl species
Shibata, N. 2010 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, USA, 2010.12. 15-20 (招待講演).
- (10) Shelf-Stable Electrophilic Trifluoromethylating Reagents
Shibata, N. 11th National Meeting on Fluorine Chemistry, China, 2010.10.13-16. (招待講演).
- (11) Synthesis and Properties of Trifluoroethoxy-Coated Subphthalocyanines
Shibata, N. 3rd Korea-Japan-China Joint Seminar on Fluorine Chemistry, Daejeon, Korea, 2010.9.9-10 (招待講演).
- (12) Enantiocontrolled Synthesis of Fluoro-organic Compounds: Building Block Approach
Shibata, N. 16th European Symposium on Fluorine Chemistry, Ljubljana, Slovenia, 2010.7.18-23 (招待講演).
- (13) Asymmetric Trifluoromethylation Reaction
Shibata, N. The Perugia Fluorine Days Symposium, Perugia, Italy, 2010.7.11-15 (招待講演).
- (14) Chiral Amplification in Enantioselective Fluorinations Using DBFOX-Ph/Metal salts
Suzuki, S.; Reddy, D. S.; Tokunaga, E.; Nakamura, S.; Shibata, N. 22nd International Symposium on Chirality (Chirality 2010; ISCD-22), Hokkaido, Japan, 2010.7.12-15 (ポスター発表).

(15) Self-disproportionation of enantiomers of the fluorinated compounds on chromatography with a non-chiral system

Nishimine, T.; Ogawa, S.; Tokunaga, E.; Nakamura, S.; Shibata, N. 22nd International Symposium on Chirality (Chirality 2010; ISCD-22), Hokkaido, Japan, 2010.7.12-15 (ポスター発表).

(16) Trifluoroethoxy-Coated Subphthalocyanines: Synthesis, Characterization, Reactivity and Solubility (招待講演).

Shibata, N. Sixth International Conference on Porphyrins and Phthalocyanines (ICPP-6), New Mexico USA, 2010.7.4-9 (招待講演).

(17) Enantiocontrolled Synthesis of Fluoro-organic Compounds

Shibata, N. Catalytic Asymmetric Synthesis-2010, Beijing, China, 2010.5.19-21 (招待講演).

3. 特許

(1) トリフルオロメチルメチオニン及びそれらの誘導体の簡便合成方法

国立大学法人名古屋工業大学, 柴田哲男, 安井宏有貴

12/801717, 2010.6.22

(2) トリフルオロメチルチオフェニウム誘導体塩, その製造方法並びにそれを用いたトリフルオロメチル基含有化合物類の製造法

国立大学法人名古屋工業大学 東ソー・エフテック株式会社, 柴田哲男

PCT/JP2010/004518, 2010.7.13

4. 学会・シンポジウム等の開催状況

なし

5. 受賞等

(1) 河合洋幸 (博士1年)

VIP 賞 第41回中部化学関係学協会支部連合秋季大会, 2010.11.6,7

(2) 森 悟 (学部4年)

最優秀ポスター賞 第25回農薬デザイン研究会, 2010.11.5

6. 新聞報道等

研究戦略 YAKU 学 No.17—研究現場から臨床へ— フッ素薬学—神ができなかったことに挑戦？

柴田哲男，薬事日報，2011.2.14

7. 領域内の共同研究の準備・実施状況とその成果

(1) 同研究共先：京都大学，吉田研究室（A01 班，計画班員）

派遣人員（受入）：森悟（学部4年）

派遣期間（受入）：2011.2.20-2011.3.13

共同研究内容：フローマイクロリアクターシステムを用いた Diphenylthioacetal の脱プロトン化

共同研究成果：未発表

8. その他特記事項

なし