

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) 不活性  $sp^3$ -C-H 結合の化学変換—触媒設計によるチャレンジ  
川守田創一郎, 澤村正也\*, 化学, **2013**, 68, 72–73.
- (2) Copper-Catalyzed  $\gamma$ -Selective and Stereospecific Direct Allylic Alkylation of Terminal Alkynes: Synthesis of Skipped Enynes.  
Makida, Y.; Takayama, Y.; Ohmiya, H.\*; Sawamura, M.\* *Angew. Chem. Int. Ed.* **2013**, 52, in press: DOI: 10.1002/anie.201300785.
- (3) Synthesis of Primary and Secondary Alkylboronates through Site-Selective C( $sp^3$ )-H Activation with Silica-Supported Monophosphine-Ir Catalysts.  
Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M.\* *J. Am. Chem. Soc.* **2013**, 135, 2947–2950.
- (4) Construction of Eight-Membered Carbocycles via Gold Catalysis with Acetylene-Tethered Silyl Enol Ethers.  
Iwai, T.; Okochi, H.; Ito, H.; Sawamura, M.\* *Angew. Chem. Int. Ed.* **2013**, 52, 4239–4242.
- (5) Use of a Semihollow-Shaped Triethynylphosphane Ligand for Efficient Formation of Six- and Seven-Membered Ring Ethers through Gold(I)-Catalyzed Cyclization of Hydroxy-Tethered Propargylic Esters.  
Ito, H.; Harada, A.; Ohmiya, H.; Sawamura, M.\* *Adv. Synth. Catal.* **2013**, 355, 647–652.
- (6) Copper-Catalyzed Enantioselective Allylic Substitution with Alkylboranes.  
Shido, Y.; Yoshida M.; Tanabe, M.; Ohmiya, H.\*; Sawamura, M.\* *J. Am. Chem. Soc.* **2012**, 134, 18573–18576.
- (7) Conjugate Reduction of  $\alpha,\beta$ -Unsaturated Carbonyl and Carboxyl Compounds with Poly(methylhydrosiloxane) Catalyzed by a Silica-Supported Compact Phosphane-Copper Complex.  
Kawamorita, S.; Yamazaki, K.; Ohmiya, H.; Iwai, T.; Sawamura, M.\* *Adv. Synth. Catal.* **2012**, 354, 3440–3444.
- (8) Rh-Catalyzed Borylation of *N*-Adjacent C( $sp^3$ )-H Bonds with a Silica-Supported Triarylphosphine Ligand.  
Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M.\* *J. Am. Chem. Soc.* **2012**, 134, 12924–12927.

- (9) Synthesis of Allenylsilanes through Copper-Catalyzed  $\gamma$ -Selective Coupling between  $\gamma$ -Silylated Propargylic Phosphates and Alkylboranes.  
Yokobori, U.; Ohmiya, H.;\* Sawamura, M.\* *Organometallics* **2012**, *31*, 7909-7913.
- (10) Enantioselective Conjugate Addition of Alkylboranes Catalyzed by a Copper-*N*-Heterocyclic Carbene Complex.  
Yoshida, M.; Ohmiya, H.;\* Sawamura, M.\* *J. Am. Chem. Soc.* **2012**, *134*, 11896–11899.
- (11) Reversible 1,3-*Anti/Syn* Stereochemical Courses in Copper-Catalyzed  $\gamma$ -Selective Allyl-Alkyl Coupling between Chiral Allylic Phosphates and Alkylboranes.  
Nagao, K.; Yokobori, U.; Makida, Y.; Ohmiya, H.;\* Sawamura, M.\* *J. Am. Chem. Soc.* **2012**, *134*, 8982–8987.
- (12) Practical Procedure for Copper(I)-Catalyzed Allylic Boryl Substitution with Stoichiometric Alkoxide Base.  
Ito, H.;\* Miya, T.; Sawamura, M. *Tetrahedron* **2012**, *68*, 3423–3427.
- (13) Functional Group Tolerable Synthesis of Alkylsilanes through Copper-Catalyzed  $\gamma$ -Selective Allyl-Alkyl Coupling between Allylic Phosphates and Alkylboranes.  
Nagao, K.; Ohmiya, H.;\* Sawamura, M.\* *Synthesis* **2012**, *44*, 1535–1541.
- (14) Regio- and Stereocontrolled Introduction of Secondary Alkyl Groups to Electron-Deficient Arenes through Copper-Catalyzed Allylic Alkylation.  
Makida, Y.; Ohmiya, H.;\* Sawamura, M.\* *Angew. Chem. Int. Ed.* **2012**, *51*, 4122–4127.
- (15) Synthesis of Conjugated Allenes through Copper-Catalyzed  $\gamma$ -Selective and Stereospecific Coupling between Propargylic Phosphates and Aryl- or Alkenylboronates.  
Yang, M.; Yokokawa, N.; Ohmiya, H.;\* Sawamura, M.\* *Org. Lett.* **2012**, *14*, 816–819.
- (16) Copper(I)-Catalyzed Allylic Substitution of Silyl Nucleophiles through Si-Si Bond Activation.  
Ito, H.;\* Horita, M.; Sawamura, M. *Adv. Synth. Catal.* **2012**, *354*, 813–817.
- (17) Efficient Preparation of  $\beta$ -Branched  $\gamma,\delta$ -Unsaturated Esters through Copper-Catalyzed Allylic Alkylation of Ketene Silyl Acetal.  
Li, D.; Ohmiya, H.;\* Sawamura, M.\* *Synthesis*. **2012**, *44*, 1304–1307.

## 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) Site-Selective Borylation of Unactivated Internal C(sp<sup>3</sup>)-H Bonds Catalyzed by Rh or Ir Complexes with Silica-Supported Monophosphine Ligands.  
Murakami, R.; Kawamorita, S.; Iwai, T.; Sawamura, M. The 7th International Conference on Cutting-Edge Organic Chemistry in Asia (ICCEOCA-7), Singapore, 2012.12.11–14 (招待講演) .

(2) Rh- or Ir-Catalyzed N-Directed Borylation of Unactivated C(sp<sup>3</sup>)-H Bonds with Silica-Supported Monophosphine Ligands.

Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M. The Twelfth International Kyoto Conference on New Aspect of Organic Chemistry (IKCOC-12), Kyoto, 2012.11.12–16 (ポスター発表) .

(3) Copper-Catalyzed  $\gamma$ -Selective and Stereospecific Direct Allylic Alkylation of Terminal Alkynes.

Takayama, Y.; Makida, Y.; Ohmiya, H.; Sawamura, M. The Twelfth International Kyoto Conference on New Aspect of Organic Chemistry (IKCOC-12), Kyoto, 2012.11.12–16 (ポスター発表) .

(4) Silica-Supported Tripod Triarylphosphines: Synthesis and Use for Preparation of Highly Active Pd Catalysts Enabling Room Temperature Cross-Coupling Reactions of Chloroarenes.

Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. The Twelfth International Kyoto Conference on New Aspect of Organic Chemistry (IKCOC-12), Kyoto, 2012.11.12–16 (ポスター発表) .

(5) Construction of Medium-Sized Rings through Gold-Catalyzed Cyclizations of Acetylenic Silyl Enol Ethers: Impact of Ligand Cavity Sizes.

Iwai, T.; Okochi, H.; Ito, H.; Sawamura, M. The 6th International Conference on Gold Science Technology and its Applications (GOLD 2012), Tokyo, 2012.9.5–8 (口頭発表) .

(6) Enantioselective Alkynylation of Aldehydes Based on Cooperative Catalysis of Copper-Chiral Hydroxy Amino Phosphine Complexes.

Ishii, T.; Watanabe, R.; Moriya, T.; Ohmiya, H.; Mori, S.; Sawamura, M. XXV International Conference on Organometallic Chemistry (ICOMC 2012), Lisbon, Portugal, 2012.9.2–7 (ポスター発表) .

(7) Rh-Catalyzed Direct Borylation of N-Adjacent C(sp<sup>3</sup>)-H Bonds with Silica-Supported Cage-Type Triaryl Monodentate Phosphine Ligand.

Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. XXV International Conference on Organometallic Chemistry (ICOMC 2012), Lisbon, Portugal, 2012.9.2–7 (ポスター発表) .

(8) Regio- and Stereocontrolled Introduction of Secondary Alkyl Groups to Electrondeficient Arenes through Copper-Catalyzed Direct Allylic Alkylation.

Makida, Y.; Ohmiya, H.; Sawamura, M. XXV International Conference on Organometallic Chemistry (ICOMC 2012), Lisbon, Portugal, 2012.9.2–7 (ポスター発表) .

(9) Enantioselective Metal Catalysis with Cooperative Hydrogen Bonds in Protic Solvents: Copper-Catalyzed Carbonyl Alkynylation with Terminal Alkynes.

Sawamura, M. 2012 Hokkaido University & Peking University Joint Symposium on Organic and Organometallic Chemistry, Sapporo, July 17, 2012.7.17 (招待講演) .

(10) Design of Cooperative Catalysis with Copper and Alcoholic Brønsted Acid Site for Enantioselective Alkynylation of Aldehydes and Keto Esters.

Sawamura, M. BIT's 3<sup>rd</sup> Annual World Congress of Catalytic Asymmetric Synthesis-2012, Beijing, China, May 12-14, 2012.5.12-14 (招待講演) .

### 3. 特許

(1) 有機高分子三点架橋型ホスフィン、それを配位子とする遷移金属錯体および触媒  
国立大学法人北海道大学, 澤村正也、岩井智弘、原田友哉  
特開 2013-045650, 2013.3.7.

### 4. 学会・シンポジウム等の開催状況

該当なし

### 5. 受賞等

(1) 澤村正也 (A01 班 公募班員)

Asian Core Program Lectureship Award, 2012.12.14.

(2) 川守田創一郎 (博士3年)

ポスター賞、第59回有機金属化学討論会, 2012.9.13-15.

(3) 長尾一哲 (修士2年)

優秀ポスター賞、第24回万有札幌シンポジウム、2012.7.7.

### 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

該当なし