

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) Ruthenium-Catalyzed Ortho-Selective Aromatic C–H Alkenylation with Alkenyl Carbonates.
Ogiwara, Y.; Kochi, T.; Kakiuchi, F.* *Chem. Lett.* in press.
- (2) Ruthenium-Catalyzed *ortho*-Selective C–H Alkenylation of Aromatic Compounds with Alkenyl Esters and Ethers.
Ogiwara, Y.; Tamura, M.; Kochi, T.; Matsuura, Y.; Chatani, N.; Kakiuchi, F.* *Organometallics* **2014**, *33*, 402-420. (10.1021/om401204h)
- (3) Copper-Catalyzed Electrochemical Chlorination of 1,3-Dicarbonyl Compounds Using Hydrochloric Acid.
Tsuchida, K.; Kochi, T.; Kakiuchi, F.* *Asian J. Org. Chem.* **2013**, *2*, 2088-2092. (10.1002/ajoc.201300168)
- (4) Rhodium-Catalyzed Dimerization of Arylacetylenes and Addition of Malonates to 1,3-Enynes.
Mochizuki, K.; Sakai, K.; Kochi, T.; Kakiuchi, F.* *Synthesis* **2013**, *45*, 2088-2092. (10.1055/s-0033-1338471)
- (5) Ruthenium-Catalyzed Reductive Deamination and Tandem Alkylation of Aniline Derivatives
Koreeda, T.; Kochi, T.; Kakiuchi, F. *J. Organomet. Chem.* **2013**, *741-742*, 148-152. (10.1016/j.jorganchem.2013.06.001)
- (6) Rhodium-Catalyzed Intermolecular [2+2] Cycloaddition to Terminal Alkynes with Electron-Deficient Alkenes.
Sakai, K.; Kochi, T.; Kakiuchi, F.* *Org. Lett.* **2013**, *15*, 1024-1027. (10.1021/ol303510k)
- (7) Catalytic Electrochemical C–H Iodination and One-Pot Arylation by ON/OFF Switching of Electric Current
Aiso, H.; Kochi, T.; Mutsutani, H.; Tanabe, T.; Nishiyama, S.; Kakiuchi, F.* *J. Org. Chem.* **2012**, *77*, 7718-7724. (10.1021/jo3012286)
- (8) Regioselective C–H Bond Cleavage/Alkyne Insertion under Ruthenium Catalysis
Hashimoto, Y.; Hirano, K.; Satoh, T.; Kakiuchi, F.*; Miura, M.* *J. Org. Chem.* **2013**, *638-646*. (10.1021/jo3025237)
- (9) Ruthenium-Catalyzed Arylation of Fluorinated Aromatic Ketones via *ortho*-Selective Carbon-Fluorine Bond Cleavage
Kawamoto, K.; Kochi, T.; Sato, M.; Mizushima, E.; Kakiuchi, F.* *Tetrahedron Lett.* **2011**, *52*, 5888-5890. (10.1016/j.tetlet.2011.09.005)

- (10) Ruthenium-Catalyzed Acylation of Arylpyridines with Acyl Chlorides via ortho-Selective C-H Bond Cleavage
Kochi, T.; Tazawa, A.; Honda, K, Kakiuchi, F.* *Chem. Lett.* **2011**, *40*, 1018-1020.
(10.1246/cl.2011.1018)
- (11) Rhodium-Catalyzed anti-Markovnikov Intermolecular Hydroalkoxylation of Terminal Acetylenes Intermolecular Hydroalkoxylation of Terminal Acetylenes
Kondo, M.; Kochi, T.; Kakiuchi, F.* *J. Am. Chem. Soc.* **2011**, *133*, 32-34.
(10.1021/ol201453h)
- (12) Convenient Synthesis of Dibenzo[*a,h*]anthracenes and Picenes via C-H Arylation of Acetophenones with Arenediboronates
Kitazawa, K.; Kochi, T.; Nitani, M.; Ie, Y.; Aso, Y.; Kakiuchi, F.* *Chem. Lett.* **2011**, *40*, 300-302. (10.1246/cl.2011.300)
- (13) Room-Temperature Regioselective C-H/Olefin Coupling of Aromatic Ketones Using an Activated Ruthenium Catalyst with a Carbonyl Ligand and Structural Elucidation of Key Intermediates
Kakiuchi, F.*; Kochi, T.; Mizushima, E.; Murai, S. *J. Am. Chem. Soc.* **2010**, *132*, 17741-17750. (10.1021/ja104918f)
- (14) Control of Product Selectivity by a Styrene Additive in Ruthenium-Catalyzed C-H Arylation
Hiroshima, S.; Matsumura, D.; Kochi, T.; Kakiuchi, F.* *Org. Lett.* **2010**, *12*, 5318-5321.
(10.1021/ol102325f)
- (15) RuH₂(CO)(PPh₃)₃-Catalyzed Arylation of Aromatic Esters Using Arylboronates via C-H Bond Cleavages
Kitazawa, K.; Kotani, M.; Kochi, T.; Langeloth, M.; Kakiuchi, F.* *J. Organomet. Chem.* **2010**, *695*, 1163-1167. (10.1016/j.jorganchem.2010.01.022)

[和文雑誌]

- (1) 新展開を見せる C-H 活性化研究 — 勃興と転機, そして”C-H functionalization”へ
垣内史敏*, *化学*, **2011**, *66* (3), 25-29.
- (2) クロスカップリングで何がどう変わる
垣内史敏*, *Ohm Bulletin*, **2011**, *47*(春号), 2-4.

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) Short-synthesis of Tetrabenzocorone by Means of Catalytic Coupling of Aromatic Ketones with Arylboronates

- Kakiuchi, F., Post International Symposium on Organic Reaction, Taipei, Taiwan, 2013.11.23 (招待講演)
- (2) (8-Quinolinolato)rhodium-catalyzed Coupling of Terminal Alkynes with Electron-deficient Alkenes
Kakiuchi, F., 11th International Symposium on Organic Reaction, Taipei, Taiwan, 2013.11.21(招待講演)
- (3) Ruthenium-Catalyzed Aromatic C-H Alkenylation Using Alkenyl Esters
Kakiuchi, F., National Taiwan University Seminar, Taipei, Taiwan, 2013.11.18 (招待講演)
- (4) (Quinolinolato)rhodium-catalyzed Couplings of Alcohols and Secondary Amines with Terminal Alkynes
Kakiuchi, F., 15th Asian Chemical Congress, Resort World Sentosa, Singapore, 2013.8.20 (招待講演)
- (5) Convenient Syntheses of Multi-substituted Acenes by C-H Functionalization
Kakiuchi, F., 16th International Symposium Homogeneous and Heterogeneous Chemistry, 北海道大学, 札幌, 2013.8.7 (招待講演)
- (6) Catalytic Arylations of Aromatic Compounds via Unreactive Bond Cleavage and Its Applications
Kakiuchi, F. 日加国際交流シンポジウム：次世代の遷移金属触媒・合成反応プロセス, 立命館大学びわこ・くさつキャンパス, 草津, 滋賀, 2013.3.23 (招待講演)
- (7) 不活性炭素-ヘテロ原子結合を利用した合成反応の開発
垣内史敏, 理研シンポジウム 第7回有機合成化学のフロンティア, 理化学研究所, 和光, 埼玉, 2012.7.6 (招待講演)
- (8) [2+2] Cycloaddition of Terminal Alkynes with Electron-Deficient Alkenes Catalyzed by 8-Quinolinolato Rhodium Complexes
Sakai, K.; Kochi, T.; Kakiuchi, F. the XXV International Conference on Organometallic Chemistry (XXV ICOMC), Lisbon, Portugal, 2012.9.4. (ポスター発表) .
- (9) Rhodium-Catalyzed Dimerization of Arylacetylenes and Cascade Additions of Active Methylene Compounds
Mochizuki, K.; Sakai, K.; Kochi, T.; Kakiuchi, F. the Twelfth International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-12), Kyoto, Japan, 2012.11.12-16 (ポスター発表) .
- (10) Synthesis of Cyclobutenes by [2+2] Cycloaddition of Terminal Alkynes with Electron-Deficient Alkenes Using 8-Quinolinolato Rhodium Catalysts

- Sakai, K.; Kochi, T.; Kakiuchi, F. the Twelfth International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-12), Kyoto, Japan, 2012.11.12-16 (ポスター発表)
- (11) Development of New Procedures of Transition Metal-Catalyzed Carbon-Heteroatom Bond Formation
Kakiuchi, F. Faculty Lecture at CNRS, Toulouse, France, 2012.3.13 (招待講演) .
- (12) Catalytic C-H Functionalization of Aromatic Ketones and Its Applications
Kakiuchi, F., International Green Catalysis Symposium: Advanced Spring School on Green Catalysis, Rennes 1 University, Rennes, France, 2012.3.7-9 (招待講演) .
- (13) Ruthenium-catalyzed Cross-couplings of Aromatic Ketones with Organoboronates via Unreactive Carbon-heteroatom Bonds Cleavage
Kakiuchi, F., Faculty Lecture at Ecole Normal de Paris, Paris, France, 2012.3.5 (招待講演)
- (14) 不活性炭素結合を利用した触媒反応の開発と利用
垣内史敏, 第8回触媒相模セミナー, 綾瀬, 神奈川, 2011.11.17 (招待講演) .
- (15) 炭素-水素結合を利用した触媒的官能基導入法の開発
垣内史敏, Green Chemistry Forum, 岡山, 岡山, 2011.10.31 (招待講演) .
- (16) Catalytic C-H Arylation of Aromatic Ketones with Arylboronates and Its Applications
Kakiuchi, F., 14th Asian Chemical Congress, Bangkok, Thailand, 2011.9.5-8 (招待講演)
- (17) Catalytic Functionalization of Aromatic Compounds *via* Carbon-Hydrogen Bond Cleavage and Its Applications
Kakiuchi, F. 14th SANKEN International Symposium 2011, 大津, 2011.1.25-26 (招待講演)
- (18) 不活性炭素結合と有機ホウ素化合物とのクロスカップリング反応
垣内史敏 第3回グリーン元素科学シンポジウム, 岡山, 2010.12.10 (招待講演)
- (19) Palladium-Catalyzed Aromatic ortho-Selective C-H Functionalization by Means of Electrochemical Oxidation
Aiso, H.; Kochi, T.; Mutsutani, H.; Nishiyama, S.; Kakiuchi, F. The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表)
- (20) Ruthenium-catalyzed Regio- selective Introduction of Carbonyl Functionality on Aromatic Ring via C-H bond Cleavage
Kakiuchi, F. Pacifichem2010, The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (招待講演)

- (21) Carbon-Nitrogen Bond Cleavage in *o*-Acyylanilines on Ruthenium Complexes and Its Relevance to Catalytic Coupling Reactions with Organoboronates
Koreeda, T.; Kochi, T.; Kakiuchi, F. The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表) .
- (22) anti-Markovnikov Hydroamination of Arylacetylenes Catalyzed by 8-Quinolinolato Rhodium Complex
Sakai, K.; Kochi, T.; Kakiuchi, F. The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表) .
- (23) Syntheses of Multi-substituted Anthracenes Using Ruthenium-catalyzed Regioselective C–H Bond Arylation
Kitazawa, K.; Kochi, T.; Kakiuchi, F. The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表) .
- (24) Convenient Synthesis of Multi-alkylated Acenes by means of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ -Catalyzed C-H Bonds Alkylation
Matsumura, D.; Kochi, T.; Kakiuchi, F. The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表) .
- (25) Ruthenium-Catalyzed Regioselective Functionalization of Aromatic C–H Bonds Using Alkenes Bearing Oxygen Leaving Groups
Ogiwara, Y.; Tamura, M.; Kochi, T.; Kakiuchi, F. The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表) .
- (26) Rhodium-Catalyzed Synthesis of Enol Ethers by anti-Markovnikov Addition of Alcohols to Terminal Arylacetylenes
Kondo, M.; Kohi, T.; Kakiuchi, F. The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表) .
- (27) Palladium-catalyzed ortho-Selective C-H Halogenation of Aromatic Compounds by Means of Electrochemical Oxidation
Aiso, H.; Kochi, T.; Kakiuchi, F. The First Symposium on Electroorganic Chemistry by Young Researchers, Keio University, Yokohama, Japan, 2010.11.27 (口頭発表)

- (28) Palladium-Catalyzed Regioselective C-H Halogenation of Arylpyridines by Means of Electrochemical Oxidation
Mutsutani, H.; Aiso, H.; Kobayashi, N.; Kochi, T.; Kakiuchi, F. China-Japan Symposium on Catalytic Organic Synthesis, Tianjin, China 2010.9.24-26 (招待講演)
- (29) Mechanistic Studies of Ruthenium-Catalyzed Cross Coupling of *ortho*-Acylanilines with Arylboronic Acid Esters
Kakiuchi, F. 24th International Conference on Organometallic Chemistry, Taipei, Taiwan, 2010.7.19 (口頭発表)

3. 特許

- (1) 芳香族化合物及びその製造法
住友化学株式会社, 学校法人慶應義塾, 垣内史敏
国際出願 WO 2010/084960, PCT/JP2010/050822, 2010年7月29日
- (2) 電気分解を利用した芳香族ハロゲン化合物の製造方法
学校法人慶應義塾, 垣内史敏
国際出願 WO 2010/104028, PCT/JP2010/053766, 2010年9月16日

4. 学会・シンポジウム等の開催状況

該当する内容はあります。

5. 受賞等

- (1) 荻原陽平 (博士2年)
学生講演賞 第92回日本化学会年会、2012.4.12
- (2) 相磯紘子 (修士2年)
ポスター賞, 近畿化学協会・有機金属化学討論会, 2011.10.14
- (3) 酒井一憲 (博士2年)
ポスター賞, 有機合成化学協会・第28回有機合成化学セミナー, 2011.9.2
- (4) 垣内史敏
Mukaiyama Award, 有機合成化学協会, 2011.8.31

6. 新聞報道等

該当する内容はあります。

7. 国民との科学・技術対話

該当する内容はあります。

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：大阪大学，三浦研究室（A03 班，公募班員）

共同研究内容：不活性炭素－水素結合を利用したアルケニル化反応の開発

共同研究成果：Regioselective C–H Bond Cleavage/Alkyne Insertion under Ruthenium Catalysis, Hashimoto, Y.; Hirano, K.; Satoh, T.; Kakiuchi, F.; Miura, M. *J. Org. Chem.* **2013**, 78, 638-646.

(2) 共同研究先：北海道大学，鈴木研究室（A03 班，計画班員）

共同研究内容：オリゴアリアル化合物を利用した環状化合物の合成

共同研究成果：ピリジン環が還元的にカップリングによりアルキル架橋ジピリジニウム環状化合物の合成を達成した。また、その分子構造を X 線構造解析により明らかにした。