

## 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) Synthesis of 7,8-Dehydropurpurin Dimers and Their Conversion to Conformationally Constrained b-to-b Vinylene-Bridged Porphyrin Dimers  
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- (2) Control of the Conformational Dynamics of *meso-meso* Vinylene-bridged Zn(II) Porphyrin Dimers through Diamine Coordination  
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- (3) Excited-State Electronic Couplings in a 1,3-Butadiyne-Bridged Zn(II)Porphyrin Dimer and Trimer  
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- (4) Facile Preparation of β-Haloporphyrins as Useful Precursors of β-Substituted Porphyrins  
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- (6) Palladium-Catalyzed Tetraarylation of 5,15-Dialkylporphyrins with Aryl Bromides  
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Ueno, R.; Fujino, D.; Yorimitsu, H.\* Osuka, A.\* *Chem. Eur. J.* **2013**, *19*, 7156–7161.

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- (22) Synthesis of a Library of Fluorescent 2-Aryl-3-trifluoromethylnaphthofurans from Naphthols by Using a Sequential Pummerer Annulation/Cross-coupling Strategy and Their Photophysical Properties  
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- (26) Palladium-Catalyzed Alkynylthiolation of Alkynes with Triisopropylsilylethynyl Sulfide  
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## 和文雑誌

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## 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）

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- (39) 機能性  $\pi$  共役系分子周辺部の時空間集積型アリール化  
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- (40) Palladium-Catalyzed Direct Arylation of Functional Aromatics  
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- (41) 機能性  $\pi$  共役系分子周辺部の直接的多重アリール化  
依光英樹 グローバル COE 第八回有機元素化学セミナー, 京都, 2011.11.21-22 (招待講演).
- (42) Palladium-Catalyzed Direct Arylation of Porphyrins  
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- (43) パラジウム触媒による複数結合の一挙構築を基盤とする新分子創製  
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- (44)  $\pi$  共役系分子の創出を指向した反応開発  
依光英樹 愛媛大学工学部応用化学科セミナー第 167 回ミニシンポジウム, 松山, 2011.7.29 (招待講演).
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- (46) Synthesis of Methylenecyclopropanes by Palladium-Catalyzed Reaction of Propargyl-Substituted Malonate Esters with Aryl Halides by Anti-Carbopalladation Pathway  
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- (47) Palladium(II)-Triggered Rearrangement of Heptaphyrins to N-Confused Porphyrins  
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(48) Cobalt-Catalyzed Benzylzincation of Alkynes

Murakami, K.; Yorimitsu, H.; Oshima, K. 16th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis, Shanghai, China, 2011.7.24-28 (ポスター発表).

(49) Synthesis of Methylenecyclopropanes by Palladium-Catalyzed Reaction of

Propargyl-Substituted Malonate Esters with Aryl Halides by Anti-Carbopalladation Pathway

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(52) Silver-Catalyzed Benzylation and Allylation of Tertiary Alkyl Bromides with

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(53) Intramolecular Reductive Addition to 2-(2,2,2,-Trifluoroethylidene)-1,3-dithiane

1-Oxide: Experimental and Theoretical Studies

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(54) Synthesis of Porphyrins Dimers by Sequential SmI<sub>2</sub>-Promoted Pinacol Coupling and

Acid-Mediated Rearrangement

Tokuji, S.; Maeda, C.; Yorimitsu, H.; Osuka, A. 5th Pacific Symposium on Radical Chemistry, Shirahama, 2011.9.25-28 (ポスター発表).

(55) Palladium-Catalyzed Direct Arylation of Porphyrins

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(56) Synthesis of Porphyrin Dimers via Pinacol Coupling–Rearrangement

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- (57) Palladium(II)-Triggered Rearrangement of Heptaphyrins to N-Confused Porphyrins  
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- (58) Synthesis of Methylenecyclopropanes by Palladium-Catalyzed Reaction of Propargyl-Substituted Malonate Esters with Aryl Halides by Anti-Carbopalladation Pathway  
Fujino, D.; Yorimitsu, H.; Oshima, K. Yonsei International Symposium on Nano-Bio Molecular Assembly, Seoul, Korea, 2011.10.27-29 (口頭発表).
- (59) Rhodium-Catalyzed Arylzincation of Terminal Allenes Providing Allylzinc Reagents and Its Application to Versatile Three-Component Coupling Reaction  
Murakami, K.; Yoshida, Y.; Yorimitsu, H.; Oshima, K. Yonsei International Symposium on Nano-Bio Molecular Assembly, Seoul, Korea, 2011.10.27-29 (口頭発表).
- (60) Unsaturated Alcohols as Surrogates of Organometallic Reagents in Palladium-Catalyzed C-C Bond Formation  
Yorimitsu, H. The Fifth Mitsui Chemicals International Symposium on Catalysis Science (MICS 2011), Kisarazu, Japan, 2011.3.9-10 (三井化学触媒科学奨励賞受賞講演).
- (61) Unsaturated Alcohols as Surrogates of Organometallic Reagents in Palladium-Catalyzed C-C Bond Formation  
Yorimitsu, H. 2011 KAIST-Kyoto University Chemistry Symposium, Kyoto, Japan, 2011.2.17-18 (招待講演).
- (62) Catalytic Allylation of Alkyl Halides with Allylic Metals Creating Quaternary Carbons  
Yorimitsu, H.; Oshima, K. The 2010 International Chemical Congress of Pacific Basin Societies (Pacificchem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (招待講演).
- (63) Pd-Catalyzed Selective Reactions Utilizing Tertiary Unsaturated Alcohols  
Yorimitsu, H. 1st International Collaborative and Cooperative Chemistry Symposium, Singapore, 2010.11.15-16 (招待講演).
- (64) Carbometalation of C-C Multiple Bonds under Cobalt, Chromium, or Rhodium Catalysis  
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- (65) Synthesis of Organophosphorus and Organosulfur Compounds via Radical Processes  
Yorimitsu, H. EUCHEM Conference on Organic Free Radicals, Bologna, Italy, 2010.6.28-7.2 (招待講演).
- (66) Palladium-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols Bearing a Trisubstituted Double Bond: Application to Chirality Transfer from Hydroxylated Carbon to Benzylic One

Wakabayashi, R.; Fujino, D.; Hayashi, S.; Yorimitsu, H.; Oshima, K. The 6th International Symposium on Integrated Synthesis (ISIS-6), Maiko Villa Kobe, Kobe, Japan , 2010.10.23-24 ( ポスター発表 ).

- (67) Rhodium-Catalyzed Arylzincation of Terminal Allenes Providing Allylzinc Reagents and Its Application to Versatile Three-Component Coupling Reaction

Yoshida, Y.; Murakami, K.; Yorimitsu, H.; Oshima, K. The 6th International Symposium on Integrated Synthesis (ISIS-6), Maiko Villa Kobe, Kobe, Japan , 2010.10.23-24 ( ポスター発表 ).

- (68) Palladium-Catalyzed Addition of Silyl-Substituted Chloroalkynes to Terminal Alkynes  
Wada, T.; Iwasaki, M.; Kondoh, A.; Yorimitsu, H.; Oshima, K. The 6th International Symposium on Integrated Synthesis (ISIS-6), Maiko Villa Kobe, Kobe, Japan , 2010.10.23-24 ( ポスター発表 ).

- (69) Silver-Catalyzed Benzylation and Allylation of Tertiary Alkyl Bromides with Organozinc Reagents

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- (70) Palladium-Catalyzed Intramolecular Carboacetoxylation of 4-Pentenyl-Substituted Malonate Esters

Fujino, D.; Yorimitsu, H.; Oshima, K. 9th International Symposium on Carbanion Chemistry (ISCC-9), Florence, Italy, 2010.7.20-24 ( ポスター発表 ).

- (71) Synthesis of Arenes Bearing a Multisubstituted Allyl Group from Aryl Halides and Homoallyl Alcohols via Palladium-Catalyzed Retro-Allylation

Iwasaki, M.; Yorimitsu, H.; Oshima, K. 9th International Symposium on Carbanion Chemistry (ISCC-9), Florence, Italy, 2010.7.20-24 ( ポスター発表 ).

- (72)  $\text{BF}_3$ -Mediated Reaction of (1-Alkynyl)dicarbonylcyclopentadienylirons with Imines:  
Exploring New Possibility of Organoiron Complexes in Organic Synthesis

Nakaya, R.; Yasuda, S.; Yorimitsu, H.; Oshima, K. 9th International Symposium on Carbanion Chemistry (ISCC-9), Florence, Italy, 2010.7.20-24 ( ポスター発表 ).

### 3 . 特許

該当無し

#### **4 . 学会・シンポジウム等の開催状況**

- (1) 10<sup>th</sup> International Symposium on Carbanion Chemistry, Kyoto, 2013.9.23–26, 依光英樹, Secretary General
- (2) ICPP 7 Satellite Symposium at Kyoto: Functions and Structures of Porphyrins and Related Molecules, Kyoto, 2012.6.29, 依光英樹, Organizing Committee Member
- (3) 5th Pacific Symposium on Radical Chemistry, Shirahama, 2011.9.25-28, 依光英樹, Secretary General

#### **5 . 受賞等**

- (1) 藤野大士 (博士3年)  
優秀ポスター賞 第60回有機金属討論会, 2013.9.12 -14.
- (2) 村上慧 (博士研究員)  
2012 Reaxys PhD Prize Finalist Elsevier, 2012.5.30
- (3) 村上慧 (博士研究員)  
学生講演賞 日本化学会第92春季年会, 2012.4.23
- (4) 藤野大士 (博士2年)  
学生講演賞 日本化学会第92春季年会, 2012.4.23
- (5) 依光英樹 (A03班, 公募班員)  
平成23年度科学技術分野の文部科学大臣表彰若手科学者賞 文部科学省、2011.4.20
- (6) 岩崎真之 (現岡山大学大学院自然科学研究科助教)  
2011 Reaxys PhD Prize Finalist Elsevier, 2011.5.26 [受賞対象の博士論文の共著者]
- (7) 村上慧 (博士3年)  
Best ChemComm Poster Prize 5th ChemComm International Symposium, 2011.5.16
- (8) 藤野大士 (博士1年)  
IUPAC Best Poster Award 16th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis, 2011.7.24-28
- (9) 依光英樹 (A03班, 公募班員)  
三井化学触媒科学奨励賞, 三井化学, 2011.3.9

#### **6 . 新聞報道等**

- (1) Asian J. Org. Chem.誌のFrontispieceとしてハイライト  
Organometallic Approaches for Direct Modification of Peripheral C-H Bonds in Porphyrin Cores. Yorimitsu, H.;\* Osuka, A.\* *Asian J. Org. Chem.* **2013**, 2, 356–373.

(2) Asian J. Org. Chem.誌の Cover としてハイライト

Direct Arylation of Porphyrin with p-Extended Aryl Bromides under Ligand-Free Fagnou-Hartwig Conditions. Yamamoto, Y.; Tokaji, S.; Tanaka, T.; Yorimitsu, H.;\* Osuka, A.\* *Asian J. Org. Chem.* **2013**, 2, 320–324.

(3) Chem. Eur. J.誌の Cover としてハイライト

Demetalation of Metal Porphyrins via Magnesium Porphyrins by Reaction with Grignard Reagents. Murakami, K.; Yamamoto, Y.; Yorimitsu, H.;\* Osuka, A.\* *Chem. Eur. J.* **2013**, 19, 9123–9126.

(4) Asian J. Org. Chem.誌の Cover としてハイライト

Amination of *meso*-Bromoporphyrins and 9-Haloanthracenes with Diarylamines Catalyzed by a Pd-PEPPSI Complex. Suzuki, Y.; Fukui, N.; Murakami, K.; Yorimitsu, H.;\* Osuka, A.\* *Asian J. Org. Chem.* **2013**, 2, 1066–1071.

(5) 低温物質科学研究センター誌の表紙としてハイライト

機能性  $\pi$  共役系分子の直接的多重アリール化 依光英樹,\* 大須賀篤弘,\* 京都大学  
低温物質科学研究センター誌, **2012**, 20, 9–17.

(6) Angew. Chem. Int. Ed.誌の Inside Cover としてハイライト

Preferential Formation of Cyclic Trimers by Palladium-Catalyzed Oxidative Coupling of 2,18-Diethynylporphyrins. Tokaji, S.; Yorimitsu, H.;\* Osuka, A.\* *Angew. Chem. Int. Ed.* **2012**, 51, 12357–12361.

(7) Chem. Eur. J.誌の Frontispiece としてハイライト

Direct Arylation of *meso*-Formyl Porphyrin. Tokaji, S.; Awane, H.; Yorimitsu, H.;\* Osuka, A.\* *Chem. Eur. J.* **2013**, 19, 64–68.

(8) 化学ウェブサイト ChemStation でのインタビュー「心に残る反応・分子を見つけてみたい」

<http://www.chem-station.com/interviews/2013/03/19.html>

(9) Most-published principal authors in Chemistry—An Asian Journal since the first issue in 2006.

Hideki Yorimitsu , *Chem. Asian J.* **2011**, 6, 4–7 , 2010.12.22

(10) **Highlighted as a Hot Paper in Angew. Chem. Int. Ed.**

Allyl-, Allenyl-, and Propargyl-Transfer Reactions through Cleavage of C–C Bonds Catalyzed by an N-Heterocyclic Carbene/Copper Complex: Synthesis of Multisubstituted Pyrroles. Sai, M.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2011**, 50, in press.

(11) **Selected by the Editorial Board of Synfacts** (*Synfacts* **2010**, 1225.)

Synthesis of 3-Trifluoromethylbenzo[*b*]furans from Phenols via Direct *Ortho* Functionalization by Extended Pummerer Reaction. Kobatake, T.; Fujino, D.; Yoshida, S.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2010**, *132*, 11838–11840.

(12) **Selected as Highlight in Org. Proc. Res. Dev.** (*Org. Proc. Res. Dev.* **2011**, *15*, 2–9.)

Synthesis of 3-Trifluoromethylbenzo[*b*]furans from Phenols via Direct *Ortho* Functionalization by Extended Pummerer Reaction. Kobatake, T.; Fujino, D.; Yoshida, S.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2010**, *132*, 11838–11840.

(13) **Selected by the Editorial Board of Synfacts** (*Synfacts* **2010**, 1037.)

Cobalt-Catalyzed Benzylzincation of Alkynes. Murakami, K.; Yorimitsu, H.; Oshima, K. *Chem. Eur. J.* **2010**, *16*, 7688–7691.

(14) **Highlighted as Synfact of the Month by the Editorial Board of Synfacts** (*Synfacts* **2010**, 1171.)

Rhodium-Catalyzed Arylzincation of Terminal Allenes Providing Allylzinc Reagents and Its Application to Versatile Three-component Coupling Reaction. Yoshida, Y.; Murakami, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2010**, *132*, 8878–8879.

(15) **Highlighted as a Featured Article by the Associate Editor of J. Org. Chem.**

Palladium-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols Bearing a Trisubstituted Double Bond: Application to Chirality Transfer from Hydroxylated Carbon to Benzylic One. Wakabayashi, R.; Fujino, D.; Hayashi, S.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2010**, *75*, 4337–4343.

(16) **Selected as Highlight in Org. Proc. Res. Dev.** (*Org. Proc. Res. Dev.* **2010**, *14*, 1276–1286.)

Palladium-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols Bearing a Trisubstituted Double Bond: Application to Chirality Transfer from Hydroxylated Carbon to Benzylic One. Wakabayashi, R.; Fujino, D.; Hayashi, S.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2010**, *75*, 4337–4343.

(17) **Selected by the Editorial Board of Synfacts** (*Synfacts* **2010**, 927.)

Nickel-Catalyzed Arylative Ring-Opening of 3-Methylenecycloalkane-1,1-dicarboxylates. Sumida, Y.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2010**, *12*, 2254–2257.

## 7. 国民との科学・技術対話

### (1) 金光学園中学高等学校夏季研修

実験実習「ヨウ素時計反応」

模擬授業「ナノの世界から原子をつないで機能を創る」

参加者 中学2年~高校3年 40名(男20名、女20名). 2013.8.19. 京都大学.

アンケート実施無.

### (2) サイエンス・カフェ高槻

「ナノの世界から原子をつないで機能を創る」

参加者 一般20名(男15名女5名). 2013.5.18. 高槻.

評価については HP <http://www.eonet.ne.jp/~scienctakatsuki/diary1.html> 参照

### (3) 金光学園高等学校サイエンスチャレンジ強化合宿

実験実習「鉄の酸化と触媒作用」

模擬授業「クロスカップリング反応～現代社会を支える有機金属化学～」

参加者高校1年生5名(男5名). 2012.10.6. 京都大学. アンケート実施無.

### (4) プレオープンキャンパス土佐高等学校 京都大学理学部化学科訪問

模擬授業「クロスカップリング反応～現代社会を支える有機金属化学～」

参加者高校1年生35名(男21名女14名). 2012.8.8. 京都大学.

アンケート実施有り. 全員が「面白かった」と回答. 「化学を好きになった」

「化学がこんなに世の中の役に立っているとは知らなかった」などの高評価多数.

## 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