

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) 2-Aryl-4-quinolone Synthesis Using the Thermal Rearrangement of Iminocyclobutenones
Hachiya, I.; Yokoyama, K.; Ito, A.; Shimizu, M. *Heterocycles* **2014**, 90, in press.
- (2) Chemoselective Reductions and Iodinations Using Titanium Tetraiodide
Hachiya, I.; Shimizu, M.* *Tetrahedron Lett.* **2014**, 55, in press.
- (3) Integrated Reactions Based on the Sequential Addition to α -Imino Esters
Koyama, K.; Mizota, I.; Shimizu, M.* *Pure Appl. Chem.* **2014**, 86, in press.
- (4) Titanium Tetraiodide Mediated Organic Reactions
Haneishi, T.; Hachiya, I.; Shimizu, M.* *Arabian J. Sci. Eng.* **2014**, 39, in press.
- (5) Chiral β -Lactam Synthesis Using Enantioselective Reduction of Iminocyclobutenones and Thermal Rearrangement of Aminocyclobutenones
Hachiya, I.; Ito, A.; Shimizu, M.* *Asian J. Org. Chem.* **2014**, 3, in press.
(10.1002/ajoc.201402005R1).
- (6) Two-Step Synthesis of 3,4-Ethylenedioxothiophene (EDOT) from 2,3-Butanedione
Hachiya, I.; Yamamoto, T.; Inagaki, T.; Matsumoto, T.; Takahashi, A.; Mizota, I.; Shimizu, M.* *Heterocycles* **2014**, 88, 607-612. (10.3987/COM-13-S(S)8).
- (7) Diastereoselective Iodo Aldol Reaction of γ -Alkoxy α,β -Alkynyl Ketone Derivatives Promoted by Titanium Tetraiodide
Hachiya, I.; Ito, S.; Kayaki, S.; Shimizu, M.* *Asian J. Org. Chem.* **2013**, 2, 931-934.
(10.1002/ajoc.201300165).
- (8) Regioselective Tandem *N*-Alkylation/*C*-Acylation of β,γ -Alkynyl α -Imino Esters
Mizota, I.; Matsuda, Y.; Kamimura, S.; Tanaka, H.; Shimizu, M.* *Org. Lett.* **2013**, 15, 4206-4209 (10.1021/ol401934x).
- (9) Synthesis of Azulene Derivatives Having an Azathiacrown Ether Moiety and Their Selective Color Reaction toward Silver Ion
Wakabayashi, S.*; Uchida, M.; Tanaka, R.; Shimizu, M. *Asian J. Org. Chem.* **2013**, 2, 786-791. (10.1002/ajoc.201300131).
- (10) Tandem *N*-Alkylation-Addition Reaction of α -Imino Esters and Application to a New Flow System
Sano, T.; Mizota, I.; Shimizu, M.* *Chem. Lett.* **2013**, 42, 995-997 (10.1246/cl.130396).
- (11) Highly Diastereoselective Tandem *N*-Alkylation-Mannich Reaction of α -Imino Esters
Shimizu, M.*; Kurita, D.; Mizota, I. *Asian. J. Org. Chem.* **2013**, 2, 208-211.

(10.1002/ajoc.201300010)

(12) A New Single-ion Polymer Electrolyte Based on Polyvinyl Alcohol for Lithium Ion Batteries

Zhu, Y. S.; Wang, X. J.; Hou, Y. Y.; Gao, X. W.; Liu, L. L.; Wu, Y. P.*; Shimizu, M. *Electrochimica Acta* **2013**, *87*, 113–118. (org/10.1016/j.electacta.2012.08.114)

(13) Synthesis of Indolin-3-ones and Tetrahydro-4-quinolones Using α -Imino Esters

Shimizu, M.*; Takao, Y.; Katsurayama, H.; Mizota, I. *Asian. J. Org. Chem.* **2013**, *2*, 130-134. (10.1002/ajoc.201200174)

(14) Synthesis of α -Amino Ketones and *O*-Alkyloximes by Titanium Tetrahalide Promoted Ring-opening Reaction of 2-Mono-substitued Azetidine-3-ones and Their *O*-Alkyloximes
Ariga, S.; Hata, S.; Fukuda, D.; Nishi, T.; Hachiya, I.; Shimizu, M.* *Heterocycles* **2012**, *86*, 1187-1210. (10.3987/COM-12-S(N)74)

(15) Synthesis of α -Dialkylamino Esters Using Tandem *N,N*-Dialylation of α -Sulfoximino Ester

Hata, S.; Maeda, T.; Shimizu, M.* *Bull. Chem. Soc. Jpn.* **2012**, *86*, 1203-1205. (10.1246/bcsj.20120195)

(16) Sulfur-Containing Pyridylazulenes: Synthesis and Chromogenic Behaviors for Heavy Metal Ions

Wakabayashi, S.*; Matsumoto, E.; Nishiguchi, M.; Yamaoka, R.; Ishiura, M.; Tsuji, M.; Shimizu, M. *Heterocycles* **2012**, *85*, 2251-2258. (10.3987/COM-12-12536)

(17) Integrated Reactions Using Addition to Conjugated Imines and Iminium Salts

Nishi, T.; Mizota, I.; Shimizu, M.* *Pure Appl. Chem.* **2012**, *84*, 2609-2617. (10.1351/PAC-CON-12-01-03)

(18) Synthesis of Nitrogen-containing Heterocycles Using Conjugate Addition Reactions of Nucleophiles to α,β -Unsaturated Imines

Hachiya, I.; Mizota, I.; Shimizu, M.* *Heterocycles* **2012**, *85*, 993-1016. (10.3987/REV-12-726)

(19) ヨウ化チタンを用いる有機分子変換反応の開発

清水 真,* 西 隆文, 溝田 功, 八谷 巍, 東海化学工業会会報 **2012**, *272*, 4-9.

(20) Synthesis of γ,δ -Unsaturated Quaternary α -Alkylamino Acids Using Umpolung Reaction and Claisen Rearrangement

Mizota, I.; Tanaka, K.; Shimizu, M.* *Tetrahedron Lett.* **2012**, *53*, 1847-1850. (10.1016/j.tetlet.2012.01.133)

(21) Regioselective Ring-opening Reaction of 2-Mono-substituted Azetidin-3-ones Promoted by the Combines Use of Titanium Tetraiodide and Its Chloro or Bromo Counterpart

- Hata, S.; Fukuda, D.; Hachiya, I.; Shimizu, M.* *Heterocycles* **2012**, *84*, 301-307.
(10.3987/COM-11-S(P)26)
- (22) Synthesis of α,α -Disubstituted α -Amino Esters: Nucleophilic Addition to Iminium Salts Generated from Amino Ketene Silyl Acetals
Hata, S.; Koyama, H.; Shimizu, M.* *J. Org. Chem.* **2011**, *76*, 9670-9677.
(org/10.1021/jo201692x)
- (23) Reductive Aminopropylation of Ketene Silyl (Thio)acetals Leading to the Synthesis of δ -Amino Esters
Mizota, I.; Agatani, S.; Hachiya, I.; Shimizu, M.* *Tetrahedron Lett.* **2011**, *52*, 5388-5391.
(10.1016/j.tetlet.2011.08.054)
- (24) Double Nucleophilic Addition Reaction to Acrolein with Ketene Silyl Acetals and Allylborolanes Catalyzed by Proline
Shimizu, M.*; Kawanishi, M.; Itoh, A.; Mizota, I.; Hachiya, I. *Chem. Lett.* **2011**, *40*, 862-863.
(10.1246/cl.2011.862)
- (25) 共役イミンおよびイミニウム塩への付加反応を基軸とする反応の集積化
波多慎吾, 清水 真, * 有機合成化学協会誌 **2011**, *69*, 1134-1144. (
- (26) Titanium Tetraiodide Promoted Reductive Enolate Formation of α -Tosyloxy Ketone Derivatives and Aldol Reaction with Aldehydes
Hachiya, I.; Inagaki, T.; Ishihara, Y.; Shimizu, M.* *Bull. Chem. Soc. Jpn.* **2011**, *84*, 419–421.
(10.1246/bcsj.20100363)
- (27) Research Progress of Gel Polymer Electrolytes for Lithium Ion Batteries
Zhang, P.; Li, L.; He, D.; Wu, Y.*; Shimizu, M. *Acta Polymerica Sinica* **2011**, 125-131.
(10.3724/SP.J.1105.2011.10229)
- (28) Efficient Mannich Reaction Using Iminium Salts Generated from Glycine Derivatives
Shimizu, M.*; Kusunoki, T.; Yoshida, M.; Kondo, K.; Mizota, I. *Chem. Lett.* **2011**, *40*, 351-353.
(10.1246/cl.2011.351)
- (29) Titanium Tetraiodide Promoted Tandem Prins Reaction of Alkynes with Acetals:
Synthesis of (*Z,Z*)-1,5-Diido-1,3,5-triarylpena-1,4-dienes
Shimizu, M.*; Okura, K.; Arai, T.; Hachiya, I. *Chem. Lett.* **2010**, *39*, 1052-1054.
(10.1246/cl.2010.1052)
- (30) Use of *N*-Allylidene-1,1-diphenylethanamine as a Latent Acrolein Synthon in the Double Nucleophilic Addition Reaction of Ketene Silyl (Thio)acetals and Allylborolanes
Shimizu, M.*; Kawanishi, M.; Mizota, I.; Hachiya, I. *Org. Lett.* **2010**, *12*, 3571-3573.
(10.1021/ol101061t)

- (31) Synthesis of 3,4-Ethylenedioxothiophene (EDOT) from (Z)-But-2-ene-1,4-diol or But-2-yne-1,4-diol
 Hachiya, I.; Matsumoto, T.; Inagaki, T.; Takahashi, A.; Shimizu, M.* *Heterocycles* **2010**, 82, 449-460. (10.3987/COM-10-S(E)16)
- (32) A New Method for the Synthesis of Multi-substituted Pyrroles of Biological Interest by Double Nucleophilic Addition to α,β -Unsaturated Imines
 Takahashi, A.; Kawai, S.; Hachiya, I.; Shimizu, M.* *Eur. J. Org. Chem.* **2010**, 191-200. (10.1002/ejoc.200901055)
- (33) Reductive Aldol and Mannich-Type Reactions of Azetidin-3-ones Promoted by Titanium Tetraiodide
 Hata, S.; Fukuda, D.; Hachiya, I.; Shimizu, M.* *Chem. Asian J.* **2010**, 5, 473-477. (10.1002/asia.200900457)
- (34) Facile Synthesis and Ring-Opening of 4-(Tributylstannylyl)pyrrolidine-2-carboxylates
 Shimizu, M.*; Ando, H.; Shibuya, H.; Hachiya, I. *Heterocycles* **2010**, 80, 773-778. (10.3987/COM-09-S(S)73)
- (35) α, β -不飽和イミンへの共役付加反応を用いる新規合成反応
 八谷 嶽、清水 真*、有機合成化学協会誌**2010**, 68, 1006-1016.

その他、査読無しの著作

- (1) Samarium(II) Iodide and Titanium(IV) Iodide
 Inanaga, J.; Shimizu, M.; Hachiya, I. In *Iodine: Chemistry and Application*; Kaiho, T., Ed; John Wiley & Sons: Hoboken, NJ, 2014; Chap. 15-4, in press.
- (2) EDOT の効率的な合成法、奥崎秀典監修 P E D O T の材料物性とデバイス応用
 清水 真、八谷 嶽、サイエンス&テクノロジー、東京、2012、pp 17-23.
- (3) ヨウ化チタンの反応、横山正孝監修 ヨウ素の化学と最新応用技術
 清水 真、八谷 嶽、シーエムシー、東京、2011、pp 183-195.
- (4) Magnesium Halides
 Shimizu, M. In *Science of Synthesis Knowledge Updates*; Ishihara, K., Ed; Thieme: Stuttgart, 2010; Vol 7, Chap. 6.12, pp 21-30.
- (5) Magnesium Oxide, Alkoxides, and Carboxylates
 Shimizu, M. In *Science of Synthesis Knowledge Updates*; Ishihara, K., Ed; Thieme: Stuttgart, 2010; Vol 7, Chap. 6.13, pp 31-40.
- (6) Magnesium Amides
 Shimizu, M. In *Science of Synthesis Knowledge Updates*; Ishihara, K., Ed; Thieme: Stuttgart, 2010; Vol 7, Chap. 6.14, pp 41-56.

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) 共役イミン誘導体を活用する新規合成反応

清水 真, 有機合成化学協会東海支部総合講演会, 岐阜薬科大学, 岐阜市, 2013.12.11 (招待講演) .

(2) Tandem *N*-Alkylation-Addition Reaction of α -Aldimino Esters and Application to a New Flow System

Sano, T.; Mizota, I.; Shimizu, M. The 8th International Symposium on Integrated Synthesis (ISIS-8), Nara, Japan, 2013.11.29-12.1 (ポスター発表) .

(3) Integrated Reactions Based on the Sequential Addition to Conjugated Imines

Shimizu, M. The 23rd International Symposium on Fine Chemistry and Functional Polymers & IUPAC 9th International Conference on Novel Materials and Their Synthesis, Shanghai, China, 2013.10.17-22 (招待講演)

(4) Umpoled Tandem Reaction of α -Imino Esters

Shimizu, M. The 15th Asian Chemical Congress (ACC15), Singapore, 2013.8.19-25 (招待講演)

(5) Unsaturated Imino Compounds as Acceptors for Multiple Nucleophiles

Shimizu, M. 1st International Symposium on Nature Product, Biotechnology and Catalysis, Hohhot, China, 2013.7.17-19 (基調講演) .

(6) Stereodivergent Synthesis of β -Lactams Using Thermal Rearrangement of Aminocyclobutenones

Hachiya, I.; Ito, A.; Shimizu, M. The 12th International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-12), Kyoto, Japan, 2012.11.12-16 (口頭発表) .

(7) 共役イミン誘導体-ハイブリッド合成素子

清水 真、第43回中部化学関係学協会支部連合秋期大会、名古屋工業大学、愛知、2012.11.10-11 (依頼講演)

(8) α -Imino Esters as Versatile Building Blocks in Organic Synthesis

Shimizu, M. The 22nd International Symposium on Fine Chemistry and Functional Polymers & IUPAC 8th International Conference on Novel Materials and Their Synthesis, Xi'An, China, 2012.10.14-19 (招待講演) .

(9) Claisen Rearrangement of α -Imino Allyl Ester Using an Umpolung Reaction

Mizota, I.; Shimizu, M. The 22nd International Symposium on Fine Chemistry and Functional Polymers & IUPAC 8th International Conference on Novel Materials and Their Synthesis, Xi'An, China, 2012.10.14-19 (ポスター発表) .

(10) Nucleophilic Addition to Conjugated Imines Leading to the Synthesis of Heterocycles

Umpoled Tandem Reaction of α -Imino Esters

Shimizu, M. 4th Congress of the European Association for Chemical and Molecular Sciences, Prague, Czech Republic, 2012.8.26-30 (招待講演) .

(11) Integrated Reactions Using Addition to Conjugated Imines

Shimizu, M. The 21st International Symposium on Fine Chemistry and Functional Polymers & IUPAC 7th International Symposium on Novel Materials and Their Synthesis, Shanghai, China, 2011.10.16-21 (招待講演) .

(12) Titanium Tetrahalides Promoted Regioselective Ring-Opening and Reductive Aldol Reaction of Azetidin-3-ones

Hata. S.; Ariga, S.; Hachiya, I.; Shimizu, M. The 21st International Symposium on Fine Chemistry and Functional Polymers & IUPAC 7th International Symposium on Novel Materials and Their Synthesis, Shanghai, China, 2011.10.16-21 (ポスター発表) .

(13) Nucleophilic Addition to Conjugated Imines Leading to the Synthesis of Heterocycles

Shimizu, M.; Hachiya, I.; Mizota, I. 14th Asian Chemical Congress, Bangkok, Thailand, 2011.9.5-8 (招待講演) .

(14) Aluminum Tetrachloride-Mediated Conjugate Addition Reaction of Ketene Silyl Acetals with Alkynyl Imines: Stereodivergent Synthesis of β -Lactams

Hachiya, I.; Yoshitomi. T.; Yamaguchi, Y.; Shimizu, M.; The 16th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS), Shanghai, China, 2011.7.24-28 (ポスター発表) .

(15) ヘテロ原子の特徴を活かしたワンポット多段階反応を基軸とする合成反応の開発

清水 真、有機合成化学協会特別賞・協会賞記念講演会、東京, 2011.2.18 (招待講演) .

(16) Umpoled Tandem Reaction of α -Imino Esters

Shimizu, M. The 2010 International Chemical Congress of Pacific Basin Societies (Pacificchem 2010), Honolulu, Hawaii, USA, 2010.12.15-20 (ポスター発表) .

(17) Intriguing Reactions Using Activated Imino Compounds

Shimizu, M. The 20th International Symposium on Fine Chemistry and Functional Polymers & IUPAC 6th International Symposium on Novel Materials and Synthesis, Wuhan, China, 2010.10.10-14 (招待講演) .

3. 特許

(1) 電解コンデンサの駆動用電解液およびそれを用いた電解コンデンサ

国立大学法人三重大学, 清水 真

特願 2013-162112, 2013. 8. 5.

(2) 電解コンデンサの駆動用電解液およびそれを用いた電解コンデンサ

国立大学法人三重大学, 清水 真

特願 2013-146611, 2013. 7. 12.

(3) 電解コンデンサの駆動用電解液及びそれを用いた電解コンデンサ

国立大学法人三重大学, 清水 真

特願 2010-144727, 2010. 6. 25

4. 学会・シンポジウム等の開催状況

- (1) The 8th International Symposium on Integrated Synthesis (ISIS-8) 東大寺総合文化センター 奈良, 2013.11.29-12.1 (清水 真, 組織委員).
- (2) The 23rd International Symposium on Fine Chemistry and Functional Polymers & IUPAC 9th International Conference on Novel Materials and Their Synthesis, Shanghai, China, 2013.10.17-22 (清水 真, 組織委員).
- (3) 1st International Symposium on Nature Product, Biotechnology and Catalysis, Hohhot, China, 2013.7.17-19 (清水 真, 組織委員).
- (4) 平成 25 年度有機合成化学協会東海支部若手研究者のためのセミナー 三重大学, 2013.7.12 (清水 真, 支部監事).
- (5) The 12th International KYOTO Conference on New Aspects of Organic Chemistry (IKCOC-12) リンガロイヤルホテル 京都、2012.12.16 (清水 真, 組織委員).
- (6) The 22nd International Symposium on Fine Chemistry and Functional Polymers & IUPAC 8th International Conference on Novel Materials and Their Synthesis, Xi'An, China, 2012.10.14-19 (清水 真, 組織委員).
- (7) 第 29 回有機合成セミナー グランシップ静岡, 2012.9.5-7 (清水 真, 組織委員).
- (8) The 21st International Symposium on Fine Chemistry and Functional Polymers & IUPAC 7th International Symposium on Novel Materials and Their Synthesis, Shanghai, China, 2011.10.16-21 (清水 真, 組織委員).
- (9) The 20th International Symposium on Fine Chemistry and Functional Polymers & IUPAC 6th International Symposium on Novel Materials and Synthesis, Wuhan, China, 2010.10.10-14 (清水 真, 組織委員)
- (10) 平成 22 年度有機合成化学協会東海支部有機合成セミナー, 三重大学, 2010.9.13 (清水 真, 支部監事).

5. 受賞等

- (1) 葛山 陽菜(修士 2 年)

優秀賞 有機合成化学協会東海支部 2013.11.20

- (2) 溝田 功 (助教)
優秀講演賞 第93日本化学会年会 2013.3.24
- (3) 溝田 功 (助教)
奨励賞 2013年度有機合成化学協会東海支部 2013.7.12
- (4) 溝田 功 (助教)
Poster Award IUPAC (Novel Materials and Their Synthesis) 2012.10.18
- (5) 有賀 静佳(修士2年)
優秀賞 有機合成化学協会東海支部 2012.11.28
- (6) 葛山 陽菜(修士1年)
優秀賞 有機合成化学協会東海支部 2012.11.28
- (7) 清水 真 (A01班, 公募班員)
有機合成化学協会賞 有機合成化学協会、2011.2.18

6. 新聞報道等

- (1) **Selected by the Editorial Board of Synfacts (Synfacts 2010, 1292.)**
Use of *N*-Allylidene-1,1-diphenylethanamine as a Latent Acrolein Synthon in the Double Nucleophilic Addition Reaction of Ketene Silyl (Thio)acetals and Allylborolanes
Shimizu, M.; Kawanishi, M.; Mizota, I.; Hachiya, I. *Org. Lett.* **2010**, *12*, 3571.

7. 国民との科学・技術対話

- (1) 「高校生のための化学講座」 対象者：高校生（男女）、参加人数：152名、
日時：平成25年8月21日、アンケート実施の有無：有、評価結果：約85%が有意義と評価
- (2) 「高校生のための化学講座」 対象者：高校生（男女）、参加人数：86名、
日時：平成24年8月17日、アンケート実施の有無：有、評価結果：約80%が有意義と評価
- (3) 「高校生のための化学講座」 対象者：高校生（男女）、参加人数：111名、
日時：平成23年8月18日、アンケート実施の有無：有、評価結果：約85%が有意義と評価
- (4) 「青少年のための科学の祭典」 対象者：小中高校生（男女）、参加人数：3, 100名、
日時：平成23年11月19、20日、アンケート実施の有無：有、評価結果：
約90%が楽しかったと回答

8. 領域内の共同研究の準備・実施状況とその成果