Academic Program [Oral B] | 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology- : Oral B

Wed. Mar 18, 2026 1:00 PM - 3:40 PM JST | Wed. Mar 18, 2026 4:00 AM - 6:40 AM UTC | F1231 (1231, Bldg. 12 [3F])

[F1231-2pm] Oral B

Chair: Harunobu Mitsunuma, Shuhei Omura

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC

[F1231-2pm-01] Construction of fused-carbocycles via hydride shift-mediated $C(sp^3)$-H bond functionalization.

○Hiroto Okawa[1], Tomoko Kawasaki-Takasuka[1], Keiji Mori[1] (1. Tokyo University of Agriculture and Technology)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC

[F1231-2pm-02] Radical Transformations of Acidic Compounds Enabled by Ketone Photocatalysis

○Hayate Sano[1], Yuki Goto[1], Hiroki Hayashi[2], Kenji Yamashita[1], Yoshitaka Hamashima[1] (1. Grad. Sch. Pharm. Sci., Univ. Shizuoka, 2. WPI-ICReDD., Hokkaido Univ.)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC

[F1231-2pm-03] Direct Ether Synthesis Utilizing the Carbonyl Umpolung Reaction

○Isao Mizota[1], Maika Yasue[1], Junya Kobayashi[1], Makoto Shimizu[1] (1. Mie University)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC

[F1231-2pm-04] Stereodefined Alkynyl Enolates Enable Asymmetric Decarboxylative Allylation toward Acyclic α-Quaternary Centers

○Shuma Sasaki[1], Jun Kikuchi[1], Naohiko Yoshikai[1] (1. Graduate School of Pharmaceutical Sciences, Tohoku University)

English
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC

[F1231-2pm-05] Silicon frustrated Lewis pairs catalyse α-deuteration of amides and esters

○Yunosuke Koga[1], Isora Fukumoto[1], Kensuke Masui[1], Tsukushi Tanaka[1], Yuki Naganawa[2], Mikihiro Hayashi[3], Takashi Ohshima[1], Ryo Yazaki[1,4] (1. Graduate School of Pharmaceutical Sciences, Kyushu University, 2. Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), 3. Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, 4. Institute for Advanced Study, Kyushu University)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC

[F1231-2pm-06] Photo-induced E/Z isomerization and site-selective transformation of diaryl oxime derivatives

○Yuki Hirata[1,2], Kosuke Higashida[2], Tatsuhiko Yoshino[2], Shigeki Matsunaga[2,1] (1. Hokkaido Univ., 2. Kyoto Univ.)

English

3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC

[F1231-2pm-07] Repurposing Fluoroform for Photocatalytic Radical Trifluoromethylation

○Yan SONG[1], Shun Zhou[2,3], Yu Harabuchi[2,3], Hitomi Katsuyama[2,3], Simon J. Cooper [2], Kosaku Tanaka, III[2,3], Tsuyoshi Mita[2,3], Satoshi Maeda[1,2,3], Hiroki Hayashi[2,3] (1. Fac. of Sci., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ., 3. JST-ERATO)

🏷 Japanese

3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC

[F1231-2pm-08] Magnesium(II) Cation–Promoted Horner–Wadsworth–Emmons Reaction Harnessing Total Syntheses of Tanzawaic Acids Q and U

○Takatsugu Murata[1], Daiki Usukura[1], Yamato Kanai[1], Ryo Hirata[1], Hisazumi Tsutsui[1], Kyohei Suzuki[1], Isamu Shiina[1] (1. Tokyo University of Science)

Construction of fused-carbocycles via hydride shift-mediated C(sp^3)–H bond functionalizations

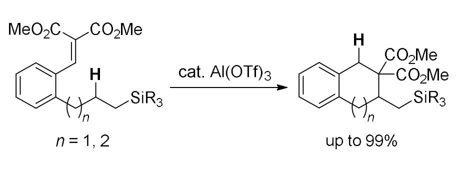
(*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○Hiroto Okawa, Tomoko Kawasaki-Takasuka, Keiji Mori

Keywords: Hydride shift; Lewis acid; C(sp^3)–H bond functionalization; divergent synthesis; redox process

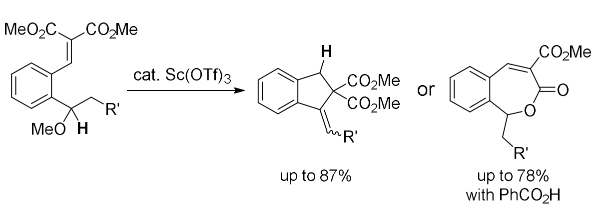
Recently, we have developed a novel synthetic method, namely, hydride shift-mediated C(sp^3)–H bond functionalization (internal redox reaction).[1] Because electronic assistance from the neighboring groups such as heteroatoms was important for the promotion of hydride shift process, the corresponding reactions at aliphatic methylene position without adjacent heteroatoms remained to be unsolved. Quite recently, we found that the target reaction was viable transformation.[2] The key to achieving this goal was the employment of substrates having silyl group β to the reacting point. Owing to the strong correlation between the stability of the carbocation generated after the hydride shift and the hydride shift capability,[3] the high β-carbocation stabilization effect of the silyl group effectively promoted the desired hydride shift from the aliphatic methylene group. Not only [1,5]-hydride shift process, but [1,6]-hydride shift process also accomplished in this reaction, giving the corresponding fused-carbocycles in good chemical yields.

During studies for the expansion of synthetic power of the above described reaction, we accidentally found another interesting synthetic method; divergent synthetic system to indanes and benzoxepines by switching of acid catalysts. When a benzylidene malonates having methoxy group at benzylic position were treated with a catalytic amount of $Sc(OTf)_3$, [1,4]-hydride shift/cyclization followed by elimination of methoxy group proceeded successively to afford *exo*-methylene-type indanes. On the other hand, benzoxepines were obtained by employing the combination of acid catalysts; $Sc(OTf)_3$ and benzoic acid. Several additional experiments and our previous results revealed that selective activation of two oxygen units (carbonyl oxygen or ether oxygen) was responsible for this divergent synthesis.

【Silyl-group supported internal redox reaction】



【Divergent synthesis of indanes and benzoxepines】



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Radical Transformations of Acidic Compounds Enabled by Ketone Photocatalysis

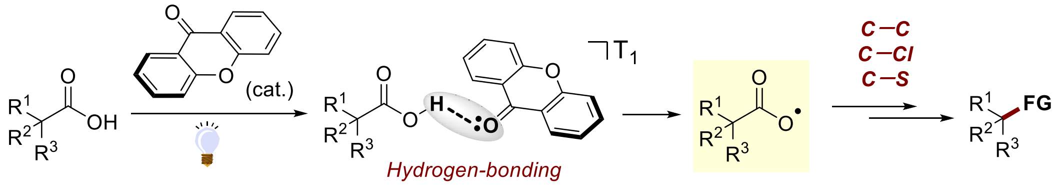
([1]*Grad. Sch. Pharm. Sci., Univ. Shizuoka*, [2]*WPI-ICReDD., Hokkaido Univ.*)
○Hayate Sano,[1] Yuki Goto,[1] Hiroki Hayashi,[2] Kenji Yamashita,[1] Yoshitaka Hamashima[1]

Keywords: Decarboxylative functionalization; *ortho*-Selective alkylation; Photocatalysis; Photoactivated ketone

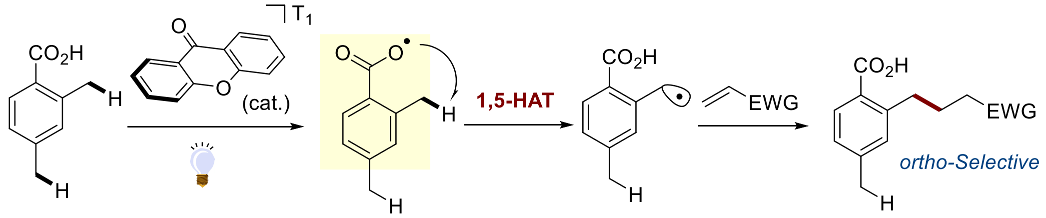
Carboxyl radicals are among the most useful open-shell species that can undergo a diverse array of valuable transformations.[1] While various catalytic methods for generating carboxyl radicals have been developed to date, they generally require stoichiometric amounts of reagents, transition-metal catalysts, or prefunctionalized redox-active esters. Herein, we present a novel photoactivated-ketone-catalyzed direct generation of carboxyl radicals via hydrogen atom transfer (HAT) from the O–H bond of carboxylic acids.[2] Owing to a hydrogen-bonding interaction between ketone and the acids, the selective O–H bond cleavage has been achieved.

This chemoselective O–H HAT enabled the decarboxylative functionalization of aliphatic carboxylic acids (Scheme A). The ketone photocatalysis for selective O–H activation was also applicable to benzoic acid derivatives, and the corresponding benzoyloxy radicals could be prepared without difficulty (Scheme B). Thus-formed benzoyloxy radicals selectively cleave the benzylic C(sp^3)–H bonds at the *ortho*-position through a 1,5-HAT mechanism. The resulting benzyl radicals then undergo a Giese-type addition to electron-deficient alkenes, providing the desired alkylated products. Furthermore, continued investigation into the photocatalytic functions of ketones has enabled radical transformations of other acidic compounds via an unprecedented reaction mechanism. These recent findings will also be presented.

A) Direct decarboxylative functionalizations



B) *ortho*-Selective C–H alkylation of benzoic acids



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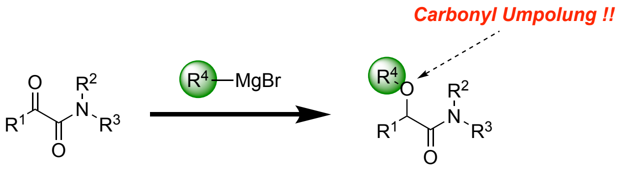
Direct Ether Synthesis Utilizing the Carbonyl Umpolung Reaction

(*Graduate School of Engineering, Mie University*) ○Isao Mizota, Maika Yasue, Junya Kobayashi, Makoto Shimizu

Keywords: α-Ketoamide; Umpolung Reaction; *O*-Alkylation; Tandem Reaction; Aldol Reaction

Ethers (R-O-R') are one of the most fundamental classes of organic compounds and are commonly found in all substances around us. Typical methods for ether synthesis include the intermolecular dehydration of alcohols and the Williamson ether synthesis. Among them, α-alkoxyamides are particularly important as they are widely found in numerous bioactive molecules such as antifungal agents (antiseptics) and PDA 10A inhibitors (antipsychotic agents), and serve as key intermediates in the synthesis of such compounds. Although various syntheses for α-alkoxyamides have been reported so far, they can be categorized into only four types: the preparation of alkoxides from α-hydroxyamides followed by the addition of alkyl halide, the Passerini reaction, the oxidation of ynamides and alcohols, and the oxidative dearomatization/oxyalkylation of indoles using a copper catalyst. To the best of our knowledge, there is no reports for direct addition to the carbonyl oxygen (*O*-alkylation).

On the other hand, our group has developed integrated reactions for nitrogen-containing compounds utilizing umpolung reactions for α-iminoesters (*N*-alkylation).[1] In 2023, we developed highly stereoselective synthesis of γ,δ-unsaturated quaternary α-aminoesters via the tandem *N*-alkylation/Claisen rearrangement of α-imino allylester.[2] Recently, the synthesis of 2*H*-1,4-oxazin-3(4*H*)-one utilizing the tandem umpolung reaction of α-hydrazonoketones followed by the reduction and cyclization were reported.[3] Herein, we found that the novel carbonyl umpolung reaction of α-ketoamides proceeded smoothly to afford the α-alkoxyamide in only one step in good to high yields. We also developed the tandem umpolung *O*-alkylation/aldol reactions with aldehydes diastereoselectively.



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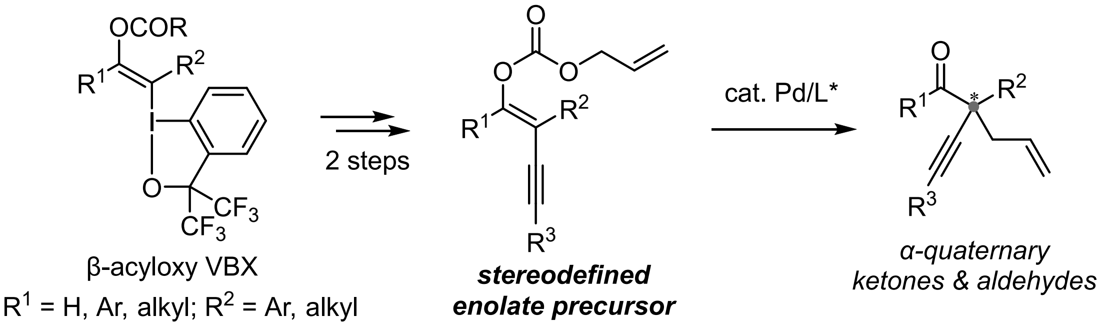
Stereodefined Alkynyl Enolates Enable Asymmetric Decarboxylative Allylation toward Acyclic α-Quaternary Centers

([1]*Graduate School of Pharmaceutical Science, Tohoku University*)
○Shuma Sasaki,[1] Jun Kikuchi,[1] Naohiko Yoshikai[1]

Keywords: Enolate; Palladium catalysis; Enantioselective allylation; Quaternary stereocenter; Hypervalent iodine

Palladium-catalyzed enantioselective allylation of multisubstituted cyclic enolates has been extensively developed as a reliable method for constructing quaternary stereocenters. In contrast, extending this strategy to acyclic systems remains challenging due to two key factors: the control of enolate C=C geometry and steric congestion around the reactive site. In particular, the former issue—intrinsic to acyclic systems—is difficult to overcome through conventional deprotonation methods. To address this limitation, we developed a method for preparing stereodefined, acyclic alkynyl enolate precursors from alkynes and demonstrated their utility in a palladium-catalyzed decarboxylative enantioselective allylation, enabling access to alkynyl-substituted acyclic quaternary stereocenters.

The stereodefined alkynyl enolate equivalents were prepared from β-acyloxyvinylbenziodoxoles (VBXs). These precursors were accessed either by iodo(III)-acetoxylation of alkynes[1] or by a 1,2-iodine(III) shift of ethynylbenziodoxoles[2]. From these VBXs, the corresponding alkynyl enolate precursors were obtained through a two-step sequence consisting of Sonogashira coupling and deacylation, followed by trapping with allyl chloroformate. These precursors underwent Pd-catalyzed enantioselective decarboxylative allylation, affording α-quaternary alkynyl ketones and aldehydes in moderate to high yields and good enantioselectivity. The critical influence of enolate geometry on enantioselectivity was confirmed by a control experiment using an enolate precursor with inverted stereochemistry. Furthermore, the carbonyl, alkynyl, and allyl functionalities in the products enabled elaboration into complex carbon frameworks.



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ケイ素 FLP 触媒を用いたアミド・エステルの触媒的 α-重水素化反応の開発

（九大院薬[1]・産総研 IRC3[2]・名工大院工[3]・九大高等研[4]）○古賀 祐之介[1]・福元 良空[1]・舛井 顕丞[1]・田中 津久志[1]・永縄 友規[2]・林 幹大[3]・大嶋 孝志[1]・矢崎 亮[1,4]

Silicon frustrated Lewis pairs catalyse α-deuteration of amides and esters

([1]*Graduate School of Pharmaceutical Sciences, Kyushu University*, [2]*Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology*, [3]*Department of Life Science and Applied Chemistry, Graduate School of engineering, Nagoya Institute of Technology*, [4]*Institute for Advanced Study, Kyushu University*) ○Yunosuke Koga,[1] Isora Fukumoto,[1] Kensuke Masui,[1] Tsukushi Tanaka,[1] Yuki Naganawa,[2] Mikihiro Hayashi,[3] Takashi Ohshima,[1] Ryo Yazaki[1,2]

Deuterium-labelled compounds play a crucial role in drug discovery as both diagnostic tools and deuterated pharmaceuticals. While hydrogen isotope exchange is well established for activated substrates, the catalytic deuteration of unactivated amides and esters remains underdeveloped, particularly under mild conditions suitable for sensitive pharmaceuticals and polymers. This limitation hampers the late-stage modification of pharmaceutical molecules and functional materials. Here we report a catalytic hydrogen isotope exchange method using cooperative catalysts—a silicon Lewis acid and a tertiary amine base—functioning as a frustrated Lewis pair. This approach enables highly selective deuteration under mild conditions. Our method achieves high deuterium incorporation in various functionalized pharmaceuticals and polyesters, including those typically unstable under basic conditions, demonstrating its broad applicability.

Keywords : Deuterium; Enolate; Frustrated Lewis Pair;

重水素は水素の非放射性安定同位体であり、創薬研究や有機合成化学をはじめとした諸分野で近年注目を集めている。しかし、アミドやエステルの α 位への直接的な H-D 交換反応としては当量以上の強塩基や高温・高圧条件を必要とする古典的手法が汎用されており、官能基許容性や環境調和性の面で課題を残していた。

種々条件検討を行なった結果、TIPSOTf を Lewis 酸、DABCO を Brønsted 塩基、Acetonitrile-d_3 を重水素源とした際に、効率的にアミド・エステルの α-重水素化反応が進行することを見出した。本反応は、天然物や医薬品、ペプチドやポリマーといった多様な化合物へ適応でき幅広い基質適用範囲を示した。さらに、機構解析実験から今回用いた Lewis 酸の TIPSOTf と Brønsted 塩基の DABCO は高反応性 Lewis 酸-塩基会合体である FLP (Frustrated Lewis Pair)を形成していることが示唆された。

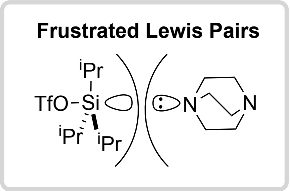

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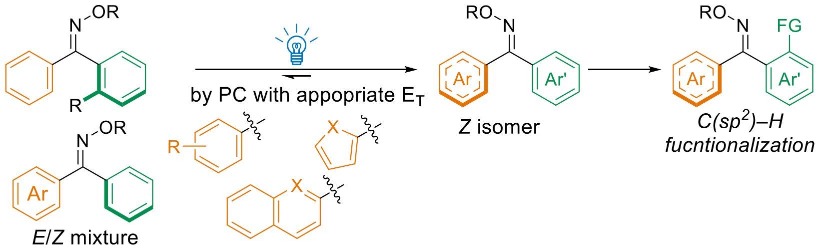
Photo-induced *E*/*Z* isomerization and site-selective transformation of diaryl oxime derivatives

([1]*Grad. Sch. Pharm. Sci. Hokkaido Univ.*, [2]*Fac. Sci., Kyoto Univ.*) ○ Yuki Hirata[1,2], Kosuke Higashida[2], Tatsuhiko Yoshino[2], Shigeki Matsunaga[1,2]

Keywords: C–H activation, photocatalysts, *E*/*Z* isomerization, site-selectivity

Oxime derivatives are versatile precursors to nitrogen-containing compounds and exist as *E*/*Z* isomers with the C=N double bond. Control of *E*/*Z* geometry is crucial for site-selective transformations of oxime derivatives.[1,2] However, selective synthesis of single isomer is challenging due to small difference of thermodynamic stability of *E*/*Z* isomers. To manipulate *E*/*Z* ratios, photoinduced *E*/*Z* isomerization using photocatalysts has been employed like alkene isomerization.[3] In this approach, a photocatalyst with an appropriate triplet energy selectively sensitizes the *E* isomer, thereby leading to accumulation of the *Z* isomer. Although Rovis and co-workers established *E*/*Z* isomerization of oxime derivatives bearing alkyl–aryl substituents,[1] aryl–aryl oximes remain challenging because the structural and electronic similarity of the *E* and *Z* isomers results in a small triplet-energy gap.[4] Herein, we report that tuning substrate conjugation with appropriate photocatalysts enables selective *E*/*Z* isomerization of diaryl oxime ethers and successive site-selective transformations.

We first examined the *E*/*Z* isomerization of an oxime ether with an *ortho*-chloro moiety using photocatalysts with various triplet energies. Screening revealed 3DPAFIPN (E_T = 54.1 kcal mol^{-1}) to be optimal, affording a high ratio of the *Z* isomer (*Z*/*E* = 1/5.0 to 14.0/1). An oxime ether bearing a 2-naphthyl group, which extends conjugation, also underwent selective isomerization with 4CzPN (E_T = 56.5 kcal mol^{-1}; *Z*/*E* = 1/1 to 12.9/1). Extending conjugation through substituent effects promoted selective *E*/*Z* isomerization, and tuning conjugation via heteroaromatic rings also proved effective. As an application of *Z*-isomer-enriched oxime ethers, we investigated site-selective C(sp^2)–H functionalization. Both C(sp^2)–H amidation and alkynylation were compatible, and the observed site-selectivities correlated with the *E*/*Z* ratios of the oxime ethers.



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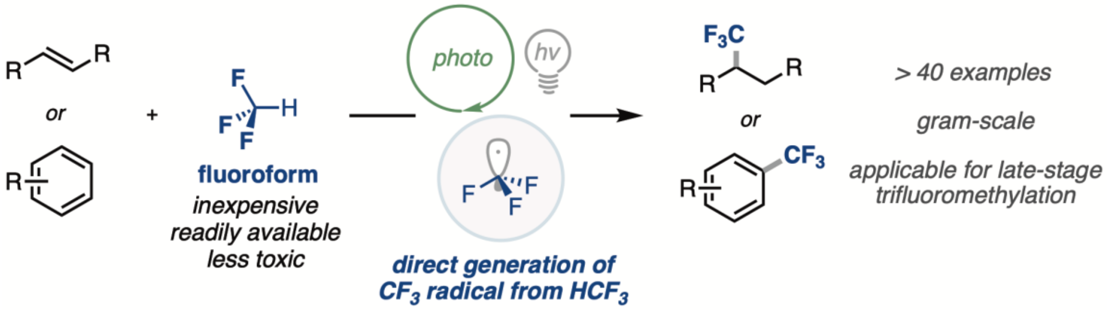
Repurposing Fluoroform for Photocatalytic Radical Trifluoromethylation

([1]*Faculty of Science, Hokkaido University*, [2]*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University*), [3]*JST, ERATO Maeda Artifical Intelligence in Chemical Reaction Design and Discovery Project, Hokkaido University* ○Yan Song,[1] Shun Zhou,[2,3] Yu Harabuchi,[2,3] Hitomi Katsuyama,[2,3] Simon J. Cooper,[2] Kosaku Tanaka III,[2,3] Tsuyoshi Mita,[2,3] Satoshi Maeda,[1,2,3] Hiroki Hayashi[2,3]

Keywords: Fluoroform; Trifluoromethylation; Radical; Photoreaction; Quantum Chemical Calculation

Radical trifluoromethylation has emerged as a powerful tool for incorporating the trifluoromethyl group directly into organic molecules to modulate their physicochemical properties in pharmaceuticals.[1] Despite its utility, radical trifluoromethylation relies on preactivated reagents, which have limitations such as high cost, handling issues including explosiveness and corrosiveness, and the generation of wasteful byproducts. Among the potential precursors, fluoroform is the inexpensive, less-toxic, and simplest trifluoromethyl-containing compound, rendering it ideal for radical trifluoromethylation; however, its practical use has been largely precluded by the exceptional thermodynamic stability of its C–H and C–F bonds, which necessitates extremely harsh conditions for direct radical generation (e.g., >600 °C).[2] Here, we report a strategy to activate fluoroform in situ for radical trifluoromethylation. The previously unexplored activation mode, guided by computational predictions, provides a photochemical system to generate trifluoromethyl radicals from fluoroform, allowing direct radical trifluoromethylation of alkenes, alkynes, and arenes. The developed method can successfully be employed in catalytic or mediator-recycling strategies, enabling the late-stage trifluoromethylation of complex molecules, or the upgrading of inexpensive materials into valuable trifluoromethylated products.



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マグネシウムイオンが促進剤として働く Horner–Wadsworth–Emmons 反応を活用したタンザワ酸 Q および U の全合成

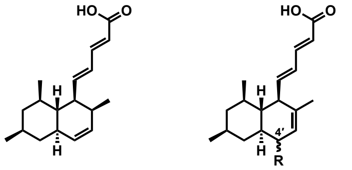
（東理大理）○村田貴嗣・臼倉大輝・金井大和・平田　諒・筒井久澄・鈴木恭平・椎名　勇

Magnesium(II) Cation–Promoted Horner–Wadsworth–Emmons Reaction Harnessing Total Syntheses of Tanzawaic Acids Q and U

(*Faculty of Science*, *Tokyo University of Science*) ○ Takatsugu Murata, Daiki Usukura, Yamato Kanai, Ryo Hirata, Hisazumi Tsutsui, Kyohei Suzuki, Isamu Shiina

In recent years, we have found that magnesium ions promote the Horner–Wadsworth–Emmons (HWE) reaction while suppressing epimerization. In this study, we utilized this property to accomplish the total syntheses of tanzawaic acids Q and U via a common octalin intermediate. The details of these findings are reported herein.

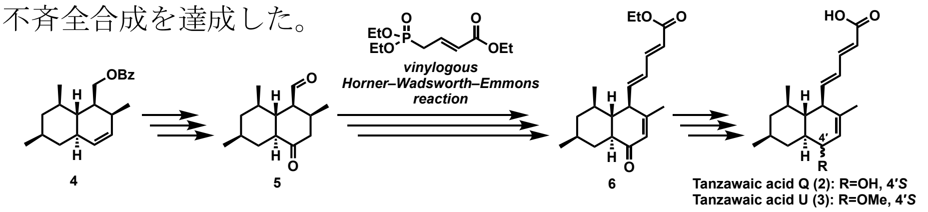
Keywords : Horner–Wadsworth–Emmons Reaction; Elongation Reaction; Tanzawaic Acid



Tanzawaic acid B (1)　Tanzawaic acid Q (2): R=OH, 4′*S*
Tanzawaic acid U (3): R=OMe, 4′*S*

タンザワ酸類はオクタリンまたはデカリン骨格とペンタジエン酸部を持つ真菌由来のポリケチド天然物である。そのうち、タンザワ酸 B (**1**)は抗菌活性を示すことが報告されている1,2)。我々は近年、オクタリン (**4**)を鍵中間体とする **1** の不斉全合成を達成した3)。また、タンザワ酸 Q, U (**2, 3**)は類似骨格を持ち、**2** は抗炎症活性を示すことが知られているが4)、両化合物ともに合成例や詳細な生物活性評価は報告されていない。そこで我々は、タンザワ酸 Q および U の全合成に取り組むこととした。

タンザワ酸 Q, U (**2, 3**)は、タンザワ酸 B (**1**)と共通の母核を有することから、**1** の全合成で用いた **4** を共通中間体とした拡散的な合成戦略を立てた。**2, 3** の合成に用いるビニロガス Horner‐Wadsworth‐Emmon 反応の際には、エピメリ化の抑制に加え、立体選択性および化学選択性を制御することが重要であった。検討の結果、マグネシウムイオンがエピメリ化を抑制しつつ目的の HWE 反応を促進することを見出した。**4** より導かれた **5** の炭素鎖伸長ならびに縮合体の官能基変換を施し、タンザワ酸 Q および U の不斉全合成を達成した。



Tanzawaic acid Q (2): R=OH, 4′*S*
Tanzawaic acid U (3): R=OMe, 4′*S*

1) Y. Morishita, K. Ando, T. Azuma, *et al.* (Kyowa Hakko Kogyo Co. Ltd.), Jpn. Pat. Appl. JPH0717939A.
2) M. Kuramoto, H. Arimoto, D. Uemura, *et al*., *Chem. Lett.*, **1997**, *26*, 885.
3) T. Murata, H. Tsutsui, I. Shiina, *et al.*, *ACS Omega*, **2023**, *8*, 27703.
4) H. J. Shin, S.-J. Heo, H. S. Won, *et al.*, *Mar. Drugs*, **2016**, *14*, 14.