



HAL
open science

Stereoselective synthesis of fissoldhimine alkaloid analogues via sequential electrooxidation and heterodimerization of ureas

Emma Naulin, Aurélien Brion, Didine Biatuma, Emmanuel Roulland, Grégory Genta-Jouve, Luc Neuville, Géraldine Masson

► **To cite this version:**

Emma Naulin, Aurélien Brion, Didine Biatuma, Emmanuel Roulland, Grégory Genta-Jouve, et al.. Stereoselective synthesis of fissoldhimine alkaloid analogues via sequential electrooxidation and heterodimerization of ureas. *Chemical Communications*, 2024, 60 (81), pp.11560-11563. 10.1039/D4CC02616K . hal-04733253

HAL Id: hal-04733253

<https://hal.science/hal-04733253v1>

Submitted on 11 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Stereoselective Synthesis of Fissoldhimine Alkaloid Analogues via Sequential Electrooxidation and Heterodimerization of Ureas.

Emma Naulin,^{‡a} Aurélien Brion,^{‡a} Didine Biatuma,^a Emmanuel Roulland,^b Grégory Genta-Jouve,^c Luc Neuville^{a,d} and Géraldine Masson^{*a,d}

^a Institut de Chimie des Substances Naturelles, CNRS, Univ. Paris-Saclay, 1 Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France.

E-mail : geraldine.masson@cnrs.fr

^b C-TAC, CitCom, UMR 8038, CNRS-Université de Paris Faculté de Pharmacie 4, avenue de l'Observatoire, 75006 Paris, France

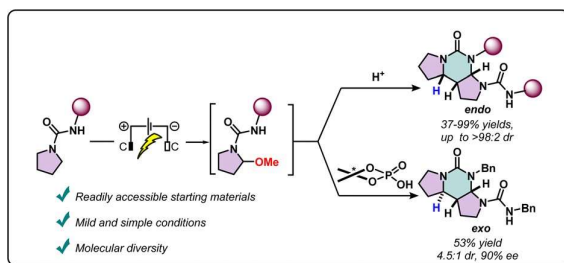
^c UAR3456 CNRS LEEISA, Centre de Recherche de Montabo, IRD, 275 Route de Montabo, CEDEX BP 70620, 97334 Cayenne, France

^d HitCat, Seqens-CNRS Joint Laboratory, Seqens' Lab, 78440 Porcheville, France

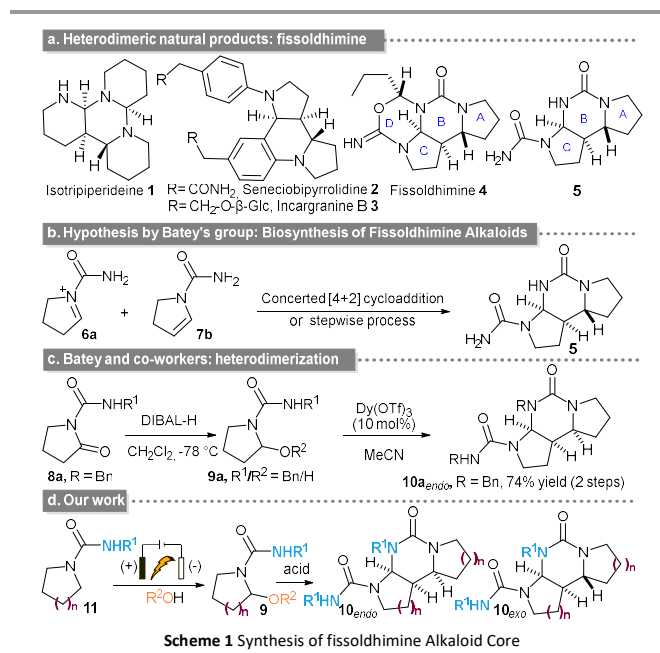
[‡] These authors contributed equally to this work

Abstract

This study develops a biogenetic synthesis strategy using electrooxidation and heterodimerization of N-substituted pyrrolidine-1-carboxamides to create diverse analogues of the fissoldhimine alkaloid core. Under acidic conditions, 2-alkoxy-pyrrolidine-1-carboxamides from Shono oxidation formed endo-heterodimers with high yields and diastereoselectivity. Enantioselective heterodimerization using chiral phosphoric acid catalysis produced exo-heterodimers with high enantioselectivity.



The biogenetic approach involving the homo- or heterodimerization of pyrrolidine and piperidine derivatives represents a significant pathway, giving rise to a broad family of natural alkaloids characterized by a wide array of biological activities.¹ Among them, fissoldhimine **4** (Scheme 1a), characterized by its tetracyclic core, was discovered by Wu *et al.* in 1994 during their isolation efforts from the perennial shrub *Fissistigma oldhamii* (Hemsl.) Merr. (Annonaceae).² Known for its various biological effects, this plant has been used in traditional medicine to treat conditions such as sciatica and arthritis. During this work, it was proposed that fissoldhimine is a chemical derivative of the natural tricyclic structure **5**, formed through aminoacetalization with adventitious butanal present in the solvent during the extraction process (Scheme 1b). In 2007, Batey and co-workers proposed a biosynthetic pathway,³ which involves the heterodimerization of *N*-carbamoyl-1-pyrrolinium **6** and *N*-carbamoyl-2-pyrroline **7**, either through an inverse electron demand Diels–Alder reaction or a two-steps process comprising a Mannich reaction followed by intramolecular amination. They explored their hypothesis by conducting the heterodimerization of alkoxy-pyrrolidine-1-carboxamides **9** in acidic conditions, yielding the tricyclic core **10** with a predominant endo selectivity, in contrast to the exo-



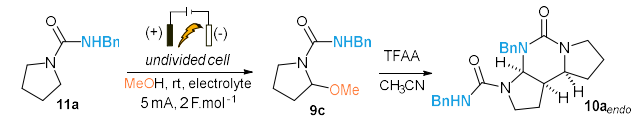
stereochemistry of the natural product **4** (Scheme 1c). In this context and based on our interest in the synthesis of azacycles,⁴ we decided to reinvestigate such heterodimerization. However, the synthesis of **9** via the protection of pyrrolidinone with isocyanate followed by reduction of amide with hydrides posed challenges.^{3,5,6} Reproducibility issues arose due to the high instability of 2-hydroxypyrrolidine-1-carboxamide **9a**, hindering product recovery during the extraction/chromatographic purification steps. Despite attempts to enhance stability by synthesizing a corresponding ether derivative **9c** (R¹/R² = Bn/Me), no improvement was observed.

To address this challenge and devise a more efficient synthetic route for **9**, we conceived an alternative approach involving the direct oxidation of pyrrolidine-1-carboxamides **11**. With the aim of establishing mild reaction conditions and drawing from our interest in organic electrochemistry,⁷ we postulated that the Shono oxidation reaction^{8,9} could effectively facilitate this transformation. This anodic oxidation process proceeds mechanistically via the 2 electrons oxidation of carbamates or amides, followed by a deprotonation step (see ESI). Since the initial studies, the Shono oxidation has witnessed extensive applications in late-stage functionalization of drug-like compounds and natural products.¹⁰ Expanded to the anodic oxidation of amines protected with sulfonyl or phosphoryl groups,¹¹ related Shono oxidation of pyrrolidine-1-carboxamides **11** remains, as far as we know, unexplored, and can pose some challenges, such as achieving chemoselective oxidation at the α-position of the tertiary nitrogen in the presence of other potentially oxidizable positions, as well as avoiding product degradation under reaction conditions. Herein we report a sequence of electrooxidation and heterodimerization of *N*-substituted pyrrolidine-1-carboxamides for stereoselective fissoldhimine alkaloid core analogues (Scheme 1d). An asymmetric version was also developed utilizing chiral phosphoric acid catalysts,¹² enabling high enantioselectivity in the dimerization process.

To study the feasibility of this anodic oxidation process, we initiated investigations utilizing *N*-benzylpyrrolidine-1-carboxamide (**11a**) as a model substrate in an undivided cell equipped with a graphite carbon plate anode and a nickel plate cathode, using anhydrous MeOH as solvent. The reaction was conducted under 10 mA constant current with LiClO₄ as the electrolyte, resulting in the formation of the desired α-methoxylated product **9c** in 73% yield. Reducing the current intensity to 5 mA resulted in an increase of yield to 90% (entry 2). Subsequent screening of various solvents yielded diminished yields (see ESI). Upon examination of various electrolytes, best results, while comparable to LiClO₄, were achieved using Bu₄NTsO (entry 4). Notably, switching the nickel plate counter electrode to a carbon graphite one with such electrolyte afforded the desired product **9c** in similar yield (entry 5). With these initial results in hand, we then decided to investigate the dimerization of **11a** in a sequential one-pot process. Regrettably, the desired product was not obtained (entry 6) when trifluoroacetic anhydride (TFAA)³ was added immediately after the electro-synthetic step. We postulated that in the present system, the possible presence of methoxide anion, released at the cathode during electrochemistry, could lead to trifluoroacetate formation instead of the required acid. Additionally, the large amount of methanol used as the solvent might inhibit the formation of iminium **6** and enamine **7**.

To address this, we evaporated the methanolic solvent and carried out the dimerization in CH₃CN in presence of TFAA. Gratifyingly, the endo-heterodimer **10a_{endo}** was isolated as a single diastereomer in 77% yield over two steps (entry 7). Additionally, only a catalytic amount of the electrolyte (0.1 eq) was necessary to achieve a 94% yield of **10a_{endo}** (entry 8) while reaching a nearly quantitative faradic efficiency.¹³ Notably, the reaction did not proceed in the absence of either electrolyte or electricity (entries 9 and 10). Further studies revealed the superiority of TFAA in term of yield and diastereoselectivity over other Brønsted and Lewis acids (*see ESI*).

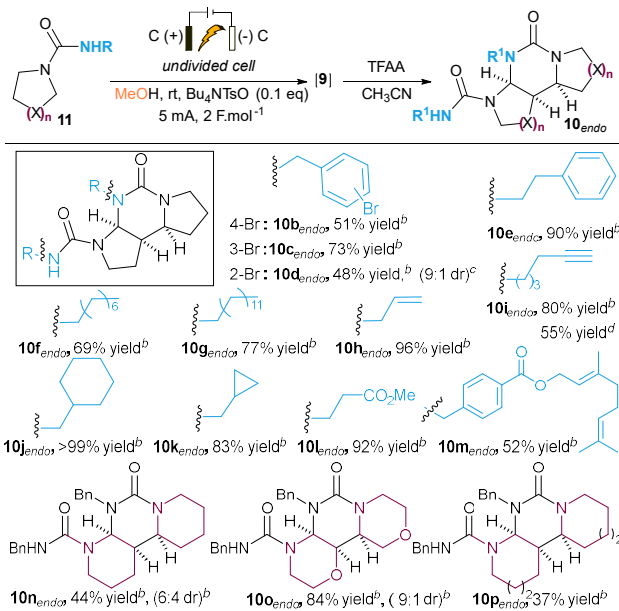
Table 1 Optimization of the reaction conditions^a



Entry	(+) / (-)	Electrolyte (eq)	Yield 9c (%) ^c	Yield 10_{endo} (%) ^d
1 ^b	(+) C / (-) Ni	LiClO ₄ (1 eq)	73	-
2	(+) C / (-) Ni	LiClO ₄ (1 eq)	90	-
3	(+) C / (-) Ni	Et ₃ NBF ₄ (1 eq)	70	-
4	(+) C / (-) Ni	Bu ₄ NTsO (1 eq)	91	-
5	(+) C / (-) C	Bu ₄ NTsO (1 eq)	91	-
6 ^e	(+) C / (-) C	Bu ₄ NTsO (1 eq)	91	0
7 ^f	(+) C / (-) C	Bu ₄ NTsO (1 eq)	91	77
8 ^f	(+) C / (-) C	Bu ₄ NTsO (0.1 eq)	99	94
9 ^g	(+) C / (-) C	Bu ₄ NTsO (0.1 eq)	-	-
10 ^h	(+) C / (-) C	Bu ₄ NTsO (0.1 eq)	-	-
11 ⁱ	(+) C / (-) C	Bu ₄ NTsO (0.1 eq)	-	81

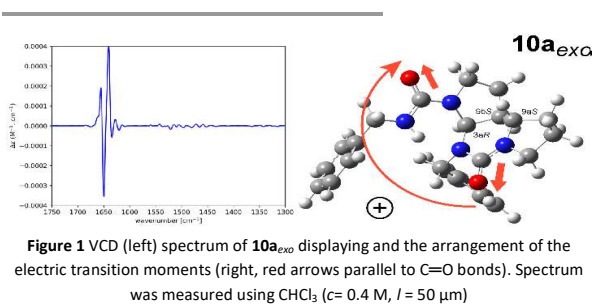
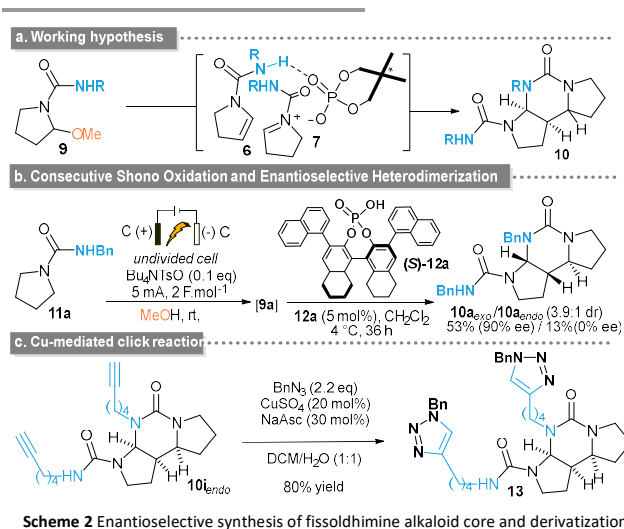
^a Conditions: **11a** (0.2 mmol), MeOH (0.05 M), 5 mA, 2 F.mol⁻¹. ^b 10 mA instead of 5 mA. ^c ¹H NMR yield using 1,1,2,2-tetrachloroethane as internal standard. ^d Isolated yield; dr > 98:2. ^e Conditions: **11a** (0.2 mmol), MeOH (0.05 M), rt., 5 mA, 2.0 F.mol⁻¹, followed by TFAA (0.2 mmol). ^f Conditions: **11a** (0.2 mmol), MeOH (0.05 M), rt, 5 mA, 2.0 F.mol⁻¹ followed by evaporation and treatment of the crude product with TFAA (0.2 mmol) in CH₃CN (0.03 M). ^g No electrolyte. ^h No electricity. ⁱ On 1 mmol, with 3 F.mol⁻¹.

Having established the optimized reaction parameters, we began to investigate the scope of this sequential process. As shown in table 2, the reaction was applicable to pyrrolidine derivatives bearing various types of substituents on the urea nitrogen atom. For instance, various benzyl substituents bearing bromine substituents positioned in *ortho*, *meta*, or *para* were accommodated, yielding the respective heterodimers, albeit with diminished yields compared to **10a_{endo}** and slightly compromised diastereoselectivity in the case of *ortho*-substitution (**10d_{endo}**). Allylic side chain was also fully compatible with the sequence delivering **10h_{endo}**, in 96% yield. Urea with a 2-phenethyl chain delivered the endo-product **10e_{endo}** in 90% yield over two steps. Linear alkyl chains, such as octyl, tridecyl, and 5-hexynyl (**10f_{endo}**, **10g_{endo}** and **10i_{endo}**) along with substituted ones like cyclopropylmethyl and cyclohexylmethyl (**10j_{endo}**-**10k_{endo}**) on the urea unit, were well-tolerated, producing the corresponding products with excellent yields ranging from 68% to 99% and excellent diastereoselectivity. Encouragingly, the urea synthesized from a geraniol derivative exhibited smooth reactivity, achieving satisfactory results in both yield and diastereoselectivity (**10m_{endo}**). Additionally, we were pleased to observe the compatibilities of functional groups such as alkene, alkyne, and ester, highlighting the mildness of this stepwise process. The scope of the reaction was expanded to include other cyclic amines. The conversion of *N*-benzylpiperidine-1-carboxamide to the desired product **10n_{endo}** was accomplished with a satisfactory yield, albeit with modest diastereoselectivity (3:2 dr). Gratifyingly, both *N*-benzylazepane-1-carboxamide and *N*-benzylmorpholine-4-carboxamide were found to be effective substrates, resulting in the formation of the corresponding heterodimeric products **10o_{endo}** and **10p_{endo}** in moderate to high yields over two-steps with a high diastereomeric ratio in favour of the endo product (9:1 to >98:2dr).

Table 2 Scope of the Shono-oxidation and heterodimerization sequence.^a

^a See entry 8, table 1 for conditions ^b Yield of isolated pure endo product after column chromatography. If unspecified, the diastereoselectivity of the crude reaction is >98/2 dr determined ¹H NMR. ^c diastereoselectivity determined by crude ¹H NMR, before purification. ^d Reaction conditions: **11** (1 mmol), MeOH (0.05 M), rt, 5 mA, $3.0 F.mol^{-1}$.

Next, we explored the feasibility of developing an enantioselective heterodimerization utilizing chiral phosphoric acid catalysts.^{4,10,14} Drawing from our own experiences and previous literature, we envisioned that the chiral Brønsted acid could facilitate the elimination of MeOH, thereby leading to the formation of an ion pair between the newly generated iminium **7** and chiral phosphate. Subsequently, its partial isomerization into enone **6**, accompanied by the formation of a hydrogen bond between the NH of the urea and the Lewis basic phosphoryl oxygen could occur (Scheme 2a). Consequently, the simultaneous interaction of the two reacting partners (**6** and **7**) by the catalyst could induce enantioselectivity during the Mannich step. To verify this hypothesis, we conducted the heterodimerization of *N*-benzyl-2-hydroxypyrrolidine-1-carboxamide **9a** in presence of chiral phosphoric acids. After examining the reaction parameters (see ESI), the reaction in CH_2Cl_2 at 0 °C with 5 mol% of catalyst (*R*)-**12a**, derived from octahydro-(*R*)-BINOL, yielded the desired heterodimer **10a** in 95% yield, predominantly as the exo product with a 4.5:1 ratio over the endo isomer. Both diastereomers were separable by column chromatography. The exo product exhibited 92% ee, demonstrating the catalyst's effectiveness in both enantio- and diastereoselectivity. The endo product was racemic, suggesting an uncatalyzed pathway. We subsequently demonstrated that it was possible to merge the Shono oxidation and enantioselective heterodimerization: under optimized conditions (involving the solvent switch). We were pleased to isolate the desired heterodimer **10a**_{exo} in 53 % with 90% ee and the racemic **10a**_{endo} in 13% yield. Importantly, there was no decline in the enantioselectivity for exo product in the consecutive process (Scheme 2b).



The determination of the absolute configuration of **10a_{exo}** was performed using vibrational circular dichroism (VCD). According to Tanigushi and Monde¹⁵, the bisignate signal of the circular dichroism reflects the absolute sense of the twist of the two electronic moments of the carbonyls. The measurement of the dihedral angle between the two carbonyl functions ($\theta = +1122^\circ$) indicated a positive exciton effect as depicted on figure 1 (two alternate Cotton negative and positive effects) allowing the absolute configuration of **10a_{exo}** to be assigned as 3*a*R, 9*a*S, 9*b*S. To the best of our knowledge, this method has never been implemented using urea's carbonyls. Therefore, we decided to ascertain our conclusion using DFT calculations (see ESI), which unambiguously confirmed the exciton coupling observed while extending the scope of the powerful method.

To evaluate the scalability of our method, we conducted the sequential electrooxidation and heterodimerization of *N*-benzylpyrrolidine-1-carboxamide (**11a**) and *N*-(hexyn-5-yl)pyrrolidine-1-carboxamide (**11i**) on a 1.0 mmol scale. The reactions proceeded with only a slight reduction in the yields of the corresponding heterodimers, **10a_{endo}** and **10i_{endo}**, (Table 1, entry 11, and Table 2). We briefly explored the post-functionalization of **10i_{endo}**, wherein a copper-catalyzed click reaction was conducted to transform the two alkyne moieties, allowing the installation of two triazole skeletons in 80% yield (Scheme 2c).¹⁶

In summary, we have devised a robust two-steps synthesis route for generating a diverse array of tricyclic azacyclic carboxamide alkans of the natural fissolhimine scaffold, starting from readily accessible cyclic carboxamides. This method involves the sequential application of Shono electrooxidation followed by acid-catalyzed heterodimerization, resulting in products exhibiting excellent yields and diastereoselectivity. By incorporating chiral phosphoric acid catalysis, we achieved the predominant formation of the *exo*-heterodimer with high enantioselectivity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

EN and AB thank Paris-Saclay University for the doctoral fellowship. We thank ICSN for the financial support.

Notes and references

- (a) E. Poupon, R. Salame, L.-H. Yan, *Biomimetic Organic Synthesis*, Wiley-VCH, Weinheim, 2011, p. 1. (b) Oleksandr O. Grygorenko, Valeriia Hutskalova, Victoria S. Moskvina, in: *Comprehensive Heterocyclic Chemistry IV*, Ed. by David StC Black, Janine Cossy, Christian V. Stevens, Elsevier, 2022, vol. 12, p. 216. (c) M.P. Mahajan, G. Bhargava, C. Mohan, in: *Comprehensive Heterocyclic Chemistry III*, Ed. by Alan R. Katritzky, Christopher A. Ramsden, Eric F.V. Scriven, Richard J.K. Taylor, Elsevier, 2008, vol. 12, p. 327. (d) H. Sato, M. Uchiyama, K. Saito and M. Yamazaki, *Metabolites*, 2018, **8**, 48.
- (a) J.-B. Wu, Y.-D. Cheng, S.-C. Kuo, T.-S. Wu, Y. Iitaka, Y. Ebizuka and U. Sankawa, *Chem. Pharm. Bull.*, 1994, **42**, 2202; (b) J. Wu, Y. Cheng, N. Chiu, S. Huang and S. Kuo, *Planta Med.*, 1993, **59**, 179.
- (a) H. Twin, W. Wen, D. Powell, A. Lough and R. Batey, *Tetrahedron Lett.*, 2007, **48**, 1841.
- Selected examples: (a) L. Jarrige, D. Glavač, G. Levitre, P. Retailleau, G. Bernadat, L. Neuville and G. Masson, *Chem. Sci.*, 2019, **10**, 3765; (b) C. Gelis, G. Levitre, J. Merad, P. Retailleau, L. Neuville and G. Masson, *Angew. Chem. Int. Ed.*, 2018, **57**, 12121; (c) T. Varlet, C. Gelis, P. Retailleau, G. Bernadat, L. Neuville and G. Masson, *Angew. Chem., Int. Ed.*, 2020, **59**, 8491; (d) T. Varlet, M. Matišić, E. Van Elslande, L. Neuville, V. Gandon and G. Masson, *J. Am. Chem. Soc.*, 2021, **143**, 11611; (e) E. Naulin, M. Lombard, V. Gandon, P. Retailleau, E. Van Elslande, L. Neuville and G. Masson, *J. Am. Chem. Soc.*, 2023, **145**, 26504.
- (a) N. Katagiri, M. Muto, M. Nomura, T. Higashikawa and C. Kaneko, *Chem. Pharm. Bull.*, 1991, **39**, 1112. (b) G. A. Swan and J.D. Wilcock, *J. Chem. Soc. Perkin Trans. 1*, 1974, 885. (c) .H. Kerr, O. Meth-Cohn, E.B. Mullock and H. Suschitzky, *J. Chem. Soc. Perkin Trans. 1*, 1974, 1614.
- Selected reviews on N,O acetals: (a) P. Wu and T. E. Nielsen, *Chem. Rev.*, 2017, **117**, 7811; (b) A. O. Kataja and G. Masson, *Tetrahedron*, 2014, **70**, 8783; (c) A. J. Basson and M. G. McLaughlin, *Tetrahedron*, 2022, **114**, 13276.
- (a) A. Claraz, C. Allain and G. Masson, *Chem. Eur. J.*, 2022, **28**, e20210337; (b) A. Claraz, A. Djian and G. Masson, *Org. Chem. Front.*, 2021, **8**, 288; (c) A. Claraz, T. Courant and G. Masson, *Org. Lett.*, 2020, **22**, 1580.
- (a) T. Shono, H. Hamaguchi and Y. Matsumura, *J. Am. Chem. Soc.*, 1975, **97**, 4264; (b) T. Shono, Y. Matsumura and K. Tsubata, *J. Am. Chem. Soc.*, 1981, **103**, 1172; (c) T. Shono, Y. Matsumura, K. Tsubata, K. Uchida, T. Kanazawa and K. Tsuda, *J. Am. Chem. Soc.*, 1984, **103**, 1172; (d) S. Asada, M. Kato, K. Asai, T. Ineyama, S. Nishi, K. Izawa and T. Shono, *J. Chem. Soc., Chem. Commun.*, 1989, 486; reviews: (e) A. M. Jones and C. E. Banks, *Beilstein J. Org. Chem.*, 2014, **10**, 3056; (f) T. Feng, S. Wang and Y. Qiu, *Synlett.*, 2022, **33**, 1582; (g) J. Yoshida, A. Shimizu and R. Hayashi, *Chem. Rev.*, 2018, **118**, 4702.
- Selected recent reviews: (a) M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.*, 2017, **117**, 13230; (b) D. S. P. Cardoso, B. Šljukić, D. M. F. Santos, C. A. C. Sequeira, *Org. Process Res. Dev.*, 2017, **21**, 1213; (c) S. Möhle, M. Zirbes, E. Rodrigo, T. Gieshoff, A. Wiebe, S. R. Waldvogel, *Angew. Chem. Int. Ed.*, 2018, **57**, 6018; (d) N. Saueremann, T. H. Meyer, Y. Qiu, and L. Ackermann, *ACS Catal.*, 2018, **8**, 7086; (f) M. D. Kärkäs, *Chem. Soc. Rev.*, 2018, **47**, 5786; (g) K. D. Moeller, *Chem. Rev.*, 2018, **118**, 4817; (h) D. Pollok and S.R. Waldvogel, *Chem. Sci.*, 2020, **11**, 12386; (i) A. Claraz and G. Masson, *ACS Org. Inorg. Au*, 2022, **2**, 126; (k) M. C. Leech and K. Lam, *Nat. Rev. Chem.*, 2022, **6**, 275. (l) C. E. Hatch, *W. J. Chain ChemElectroChem* **2023**, e202300140.
- (a) K. J. Frankowski, R. Liu, G. L. Milligan, K. D. Moeller and J. Aubé, *Angew. Chem. Int. Ed.*, 2015, **54**, 10555; (b) L. F. T. Novaes, J. S. K. Ho, K. Mao, K. Liu, M. Tanwar, M. Neurock, E. Villemure, J. A. Terrett and S. J. Lin, *J. Am. Chem. Soc.*, 2022, **144**, 1187; (c) D. K. P. Veedu, L. A. Connal and L. R. Malins *Angew. Chem. Int. Ed.*, 2023, **62**, e202215470; (d) N. R. Deprez, D. J. Clausen, J.-X. Yan, F. Peng, S. Zhang, J. Kong and Y. Bai, *Org. Lett.*, 2021, **23**, 8834; (e) M. Gausmann, N. Kreidt and M. Christmann, *Org. Lett.*, 2023, **25**, 2228; (f) Wang, M. Rafiee and S. S. Stahl, *Angew. Chem. Int. Ed.*, 2018, **57**, 6686. (g) M. A. Kabeshov, B. Musio, P. R. D. Murray, D. L. Browne and S. V. Ley, *Org. Lett.*, 2014, **16**, 4618; (h) P.-S. Gao, X.-J. Weng, Z.-H. Wang, C. Zheng, B. Sun, Z.-H. Chen, S.-L. You and T.-S. Mei, *Angew. Chem. Int. Ed.*, 2020, **59**, 15254; (i) A. G. M. Barrett and D. Pilipauskas, *J. Org. Chem.*, 1991, **56**, 2787; (j) J. Yoshida and S. Suga, *Chem. Eur. J.*, 2002, **8**, 2650.
- T. Shono, Y. Matsumura, K. Tsubata, K. Uchida, T. Kanazawa and K. Tsuda, *J. Org. Chem.*, 1984, **49**, 3711.
- Selected reviews on chiral phosphoric acid catalysis: (a) D. Parmar, E. Sugiono, S. Raja and M. Rueping, *Chem. Rev.* 2017, **117**, 10608; *Chem. Rev.* 2014, **114**, 9047; (b) J. Merad, C. Lalli, G. Bernadat, J. Maury and G. Masson. *Chem. Eur. J.* 2018, **24**, 3925; (c) E. I. Jiménez *Org. Biomol. Chem.* 2023, **21**, 3477.
- (a) M. Rafiee, M. N. Mayer, B. T. Punchedhewa and M. R. Mumau, *J. Org. Chem.*, 2021, **86**, 15866; (b) J. E. Nutting, J. B. Gerken, A. G. Stamoulis, D. L. Bruns and S. S. Stahl, *J. Org. Chem.*, 2021, **86**, 15875.
- Selected Reviews: (a) Q. Lin, L. Li and S. Luo, *Chem. Eur. J.*, 2019, **25**, 10033; (b) X. Chang, Q. Zhang and C. Guo, *Angew. Chem. Int. Ed.*, 2020, **59**, 12612; (c) M. Ghosh, V.S. Shinde and M. Rueping, *Beilstein J. Org. Chem.*, 2019, **15**, 2710.
- T. Taniguchi and K. Monde, *J. Am. Chem. Soc.* 2012, **134**, 3695.
- For additional post-manipulation, see ESI.