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Water-Mediated Catalytic Decarboxylation Enabled Polysubstituted Furans and Allylic Alcohols with Exclusive (*E*)-Configurations

Yulian Yang,[†] Linhong Zuo,[†] Kun Wei, and Wusheng Guo*

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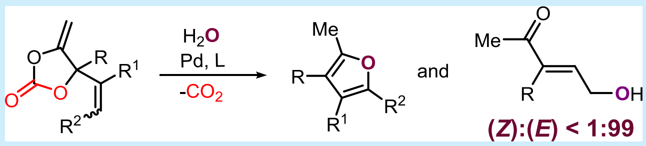
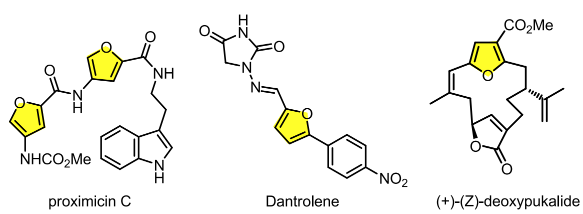
ABSTRACT: A water-mediated catalytic decarboxylation process toward the formation of polysubstituted furans and (*E*)-allylic alcohols has been reported. This protocol features wide functional group tolerance, easy operation, and only CO_2-byproduct generation. These reactions can be performed on a large scale open to air under extremely ambient conditions. A range of control experiments revealed the crucial role of the water for the successful conversions as well as the origin of the chemoselectivity and exclusive stereoselectivity.



In recent years, reducing or eliminating the use or generation of hazardous substances in chemical processes in a way that is environmentally benign is of high significance to sustainable chemistry.[1] In this respect, to develop water-mediated synthetic methodologies is interesting and of great significance for sustainable chemistry because water is readily available and nontoxic, thus serving as an ideal green reaction partner or media/solvent. However, to develop such a process in synthetic chemistry typically is not an easy task[2] because water is a very weak nucleophile and generally is extremely unreactive.

Polysubstituted furans are frequently found in pharmaceuticals, natural products, and functional materials (Scheme 1)[3] and also serve as intermediates in synthetic chemistry.[4] The design of a new catalytic system toward the efficient synthesis of furans is the continuous endeavor of synthetic chemists.[5] The synthesis of furans has advanced mainly including those of transition-metal-catalyzed intramolecular cycloisomerizations,[6] intermolecular cycloadditions,[7] and organocatalytic means,[8] while a diverse synthesis of polysubstituted furans with water as *O*-donor is quite challenging and not yet well-established. To the best of our knowledge, there is only one report[2e] with water as nucleophile for the formation of furans with quite limited substitution patterns at elevated temperatures. Therefore, to explore a water-mediated synthesis of polysubstituted furans under mild conditions is of significance especially in terms of developing sustainable chemistry.

Scheme 1. Examples of Bioactive Molecules Featuring a Furan Skeleton



On the other hand, decarboxylative chemistry has gained much research interest mainly due to the advantages of ambient reaction conditions, friendly operations, and only CO_2-byproduct generation.[9,10] Some of us previously reported that a water nucleophilic attack of a Pd-allyl intermediate derived from the decarboxylation of vinyl cyclic carbonate **A** proved to be a fantastic approach to access a batch of polysubstituted allylic alcohols with exclusive (*Z*)-configuration (Scheme 2a).[10] Taking into account the synthetically important and challenging synthesis of stereodefined polysubstituted alkenes,[11] this water nucleophilic approach[10] represents a great step forward toward (*Z*)-configured polysubstituted allylic alcohols. However, this approach could not be used for the stereoselective synthesis of the (*E*)-allylic alcohols, thus leaving this challenge unsolved. Our group very recently disclosed the cycloaddition reactions toward carbocycles and pyrroles with the use of a newly designed CO_2-derived cyclic carbonate **B** as substrates.[12] Inspired by tempting water-related chemistry,[2,10] we systematically investigated the reaction of water and this cyclic carbonate **B**. Excitingly, we found that the chemoselectivity of this water-mediated reaction could be fully controlled toward either formation of polysubstituted furans or allylic alcohols (Scheme 2b). The substitution type of the furan and allylic alcohol products could be simply modulated by varying the functional

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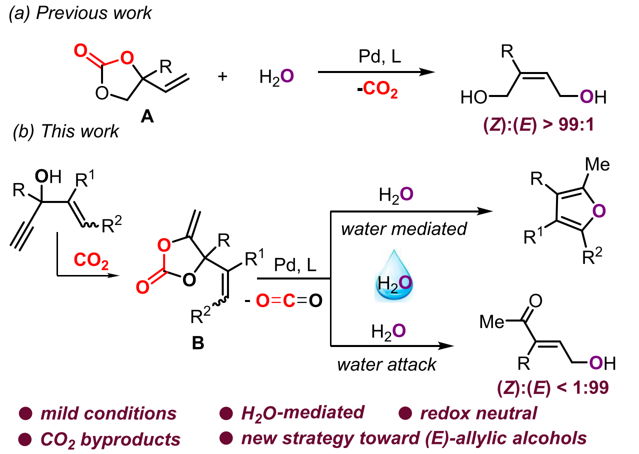
Scheme 2. Water-Mediated Pd-Catalyzed Decarboxylation of Cyclic Carbonates

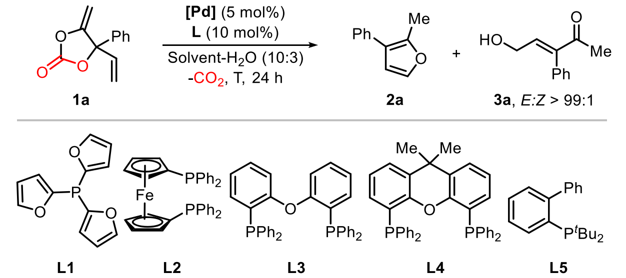


groups on the cyclic carbonates. Most importantly, by simply changing the reaction conditions, we could achieve the chemo- and stereoselective synthesis of a range of trisubstituted allylic alcohols with exclusive (E)-configuration. Herein, we reported our latest interesting results and mechanism insights on this project.

We began our study by using carbonate **1a** as the model substrate for the synthesis of furan **2a** in the presence of palladium catalyst and phosphine ligand (Table 1, entries 1–14). No conversion was observed in initial tests in different well-dried solvents (DMF, acetone, or THF), suggesting that water is crucial for the successful reaction. In the presence of $Pd(dba)_2$ and ligand **L1**, the yield of the desired furan **2a** was slightly improved when the reaction was performed at 40 °C in a mixed DMF−H_2O (10:3) (entries 1–3). The use of $Pd(TFA)_2$ precatalyst gave better results (entries 4–6). The phosphine ligand screening suggested that ligand **L4** is best toward the furan formation (entries 7–10). Gratifyingly, the reaction efficiency was greatly improved toward the selective formation of furan **2a** with the utilization of a mixture of acetone−H_2O as solvent (entries 11–14).

During our optimization process toward the formation of furan **2a**, we also found an allylic alcohol product **3a** with (E)-configuration that derived from the water nucleophilic attack. This observation is very different from previous results on Pd-catalyzed decarboxylation of vinyl cyclic carbonates.[10,12] Considering that the water nucleophilic attack reaction is challenging[2] and the synthetic importance of stereodefined allylic alcohol,[13,14] we then turned our attention for the condition screening toward the chemoselective formation of product **3a** (Table 1, entries 15–24). Changing the amount of water did not improve the reaction efficiency toward the alcohol formation (entries 15 and 16). The use of $Pd(OAc)_2$ precatalyst in the presence of **L1** in a mixed solvent of DMF−H_2O proved to be beneficial for the formation of **3a** (entry 6). To our delight, the yield of the allylic alcohol **3a** could be significantly increased to 81% when the reaction was performed at room temperature for shorter reaction time (24 vs 2 h) while keeping other conditions unchanged (entries 6 vs 17). Variation of either solvent or ligand resulted in inferior reaction outcomes (entries 18–23). In contrast, the utilization of $Pd(TFA)_2$ was much less efficient for the allylic alcohol formation (entry 24).

Table 1. Optimization of the Reaction Conditions for the Formation of Furan 2a or Allylic Alcohol 3a[a]



entry	Pd precursor	L	solvent	T (°C)	2a (%)[b]	3a[b] (%)
1	$Pd(dba)_2$	L1	DMF	25	<2	28
2	$Pd(dba)_2$	L1	DMF	40	9	45
3	$Pd(dba)_2$	L1	DMF	60	8	42
4	White catalyst	L1	DMF	40	11	44
5	$Pd(TFA)_2$	L1	DMF	40	20	51
6	$Pd(OAc)_2$	L1	DMF	40	6	60
7	$Pd(TFA)_2$	L2	DMF	40	<2	<2
8	$Pd(TFA)_2$	L3	DMF	40	7	27
9	$Pd(TFA)_2$	L4	DMF	40	23	43
10	$Pd(TFA)_2$	L5	DMF	40	<2	<2
11	$Pd(TFA)_2$	L4	CH_3CN	40	5	35
12	**$Pd(TFA)_2$**	**L4**	**acetone**	**40**	**93**	**0**
13	$Pd(TFA)_2$	L4	MeOH	40	<2	<2
14	$Pd(TFA)_2$	L4	THF	40	40	41
15[c]	$Pd(TFA)_2$	L4	acetone	40	63	<2
16[d]	$Pd(TFA)_2$	L4	acetone	40	60	<2
17[e]	**$Pd(OAc)_2$**	**L1**	**DMF**	**25**	**<2**	**81**
18	$Pd(OAc)_2$	L2	DMF	25	<2	<2
19	$Pd(OAc)_2$	L3	DMF	25	<2	<2
20	$Pd(OAc)_2$	L4	DMF	25	30	18
21	$Pd(OAc)_2$	L5	DMF	25	<2	<2
22	$Pd(OAc)_2$	L1	acetone	25	<2	20
23	$Pd(OAc)_2$	L1	MeOH	25	<2	<2
24[h]	$Pd(TFA)_2$	L1	DMF	25	25	16

[a]Reaction conditions: 0.1 mmol of carbonate **1a**, 0.1 mL of solvent. [b]^{1}H NMR yield using 2-methylnaphthalene as internal standard. [c]Acetone−H_2O (10:1) was used as solvent. [d]Acetone−H_2O (2:1) was used as solvent. [e]Entries 17–23: reactions for 2 h. [h]Quite low conversions (<3%) were observed when reaction for 2 h.

With the optimized reaction conditions in hand, we set out to investigate the generality of this water-mediated Pd-catalyzed decarboxylative transformation of cyclic carbonates **1a–1z** toward the formation of functionalized furans (Figure 1).[15] The cyclic carbonates bearing either electron-donating or -withdrawing functional groups at the *para-*, *meta-* and *ortho-*positions of the aromatic substituent reacted smoothly to afford the target furans **2a–2z** in moderate to good yields. The compatibility with the aryl halides provided the basis for the further derivatization of the products (**2f**, **2i**, **2s**). The introduction of fluorine functionality could be easily achieved (**2f–2h**, **2o**, **2s**, **2t**) in the present protocol, which is of pharmaceutical interest.[16] The clumsy naphthyl group was also tolerated (**2w**). We further note that the alkyl-substituted substrates showed satisfactory reactivity toward the target furans with good yields (**2u**, **2v**). Preinstallation of substituents on the vinyl group of the carbonate substrate enabled the preparation of tri- and tetrasubstituted (**2x**, **2y**, and **2z**) furans.

Afterward, the reaction generality toward the (E)-allylic alcohol **3** was explored (Figure 2). A range of functionalized

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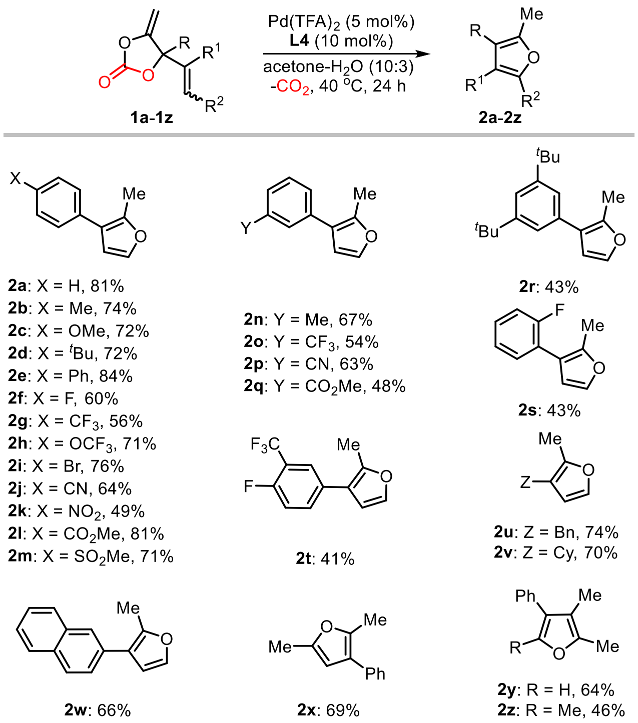

Figure 1. Carbonate scope toward the formation of furans **2a–2z**. Reaction conditions: **1** (0.20 mmol), Pd(TFA)$_2$ (5 mol %), **L4** (10 mol %), acetone–H_2O (10:3, 0.2 mL).

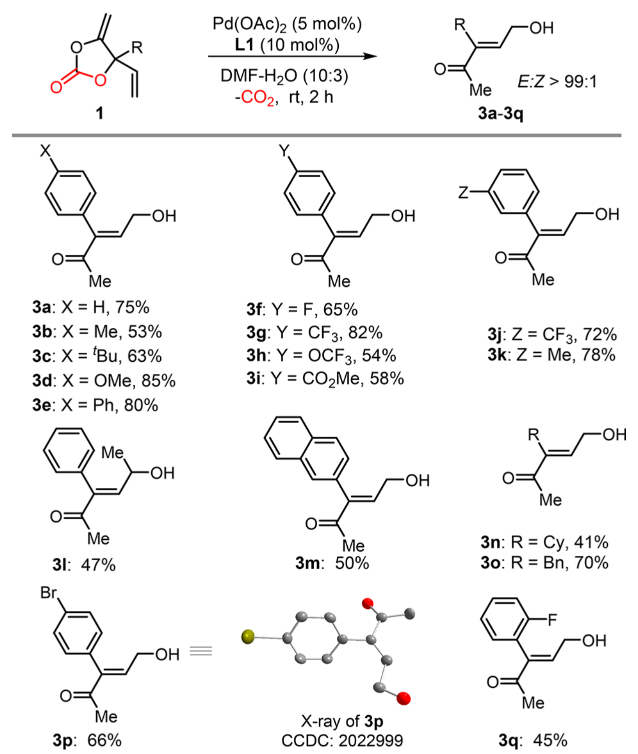

Figure 2. Carbonate scope toward the formation of (*E*)-allylic alcohol 3. Reaction conditions: carbonate **1** (0.20 mmol), Pd(OAc)$_2$ (5 mol %), **L1** (10 mol %), DMF–H_2O (10:3, 0.2 mL). Inset is the solid state of product **3p** and hydrogen atoms are omitted for clarity at 50% probability for the drawing of thermal ellipsoids.

cyclic carbonates proved to be applicable in this reaction under the optimized conditions toward otherwise synthetically challenging stereodefined allylic alcohols (**3a–3q**). The (*E*)-configuration of the allylic alcohol was unambiguously deduced from the X-ray analysis of product **3p**. The alkyl-substituted carbonates proceeded smoothly to give the corresponding products (**3n** and **3o**). It is worth mentioning that all of these reactions toward the formation of furans or (*E*)-allylic alcohols could be performed open to air under ambient conditions (rt or 40 °C), which adds further attractiveness to the present methodology. Substantial experimental work with attempts to install substituents on the exocyclic double bond was unsuccessful. The *p*-CN and NO_2-functionalized (*E*)-allylic alcohol products were indeed observed by NMR but failed in purifications though extensive experimental work has been done.

The present methodology was applicable for a larger scale reaction as exemplified in the gram-scale synthesis of furan **2e** (Figure 3a). The Friedel–Crafts acylation of **2e** afforded the 5-acetyl furan **4** in 73% yield (Figure 3b). Formylation of product **2e** could be easily achieved toward the formation of the corresponding aldehyde **5** in quantitative yield (Scheme 3b). The (*E*)-allylic alcohol framework **3** containing a *γ*-hydroxy-*α*,*β*-enone unit proved to be a useful synthetic intermediate.[14] We further showcased their synthetic application via chemoselective reduction or oxidation of the allylic alcohol **3a** while keeping the double bond intact to afford the corresponding (*E*)-1,4-but-2-enediol **6** or dicarbonyl compound **7**, respectively (Figure 3c).

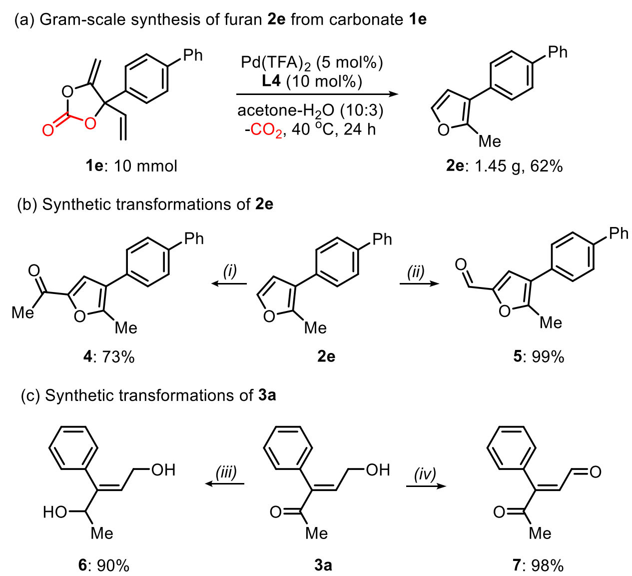

Figure 3. (a) Gram-scale synthesis of furan **2e**. (b) Synthetic transformations of **2e** under different reaction conditions: (i) AC_2O, $ZnCl_2$, rt; (ii) DMF, $POCl_3$, rt. (c) Synthetic transformations of **3a** under different reaction conditions: (iii) $CeCl_3$, $NaBH_4$, methanol, 0 °C; (iv) MnO_2, DCM, rt. See the Supporting Information for reaction details.

In order to gain more insight into the reaction regarding the chemoselectivity or the origin of the exclusive (*E*)-stereoselectivity, a series of control experiments using carbonate **1a** or **3a** as substrates were accomplished (Figure 4). No furan was observed when the reaction with carbonate **1a** as substrate was performed under the standard conditions (refer to entry 12 in Table 1) but in well-dried acetone, indicating the key role of water (Figure 4a). The addition of ^{18}O-labeled water in the

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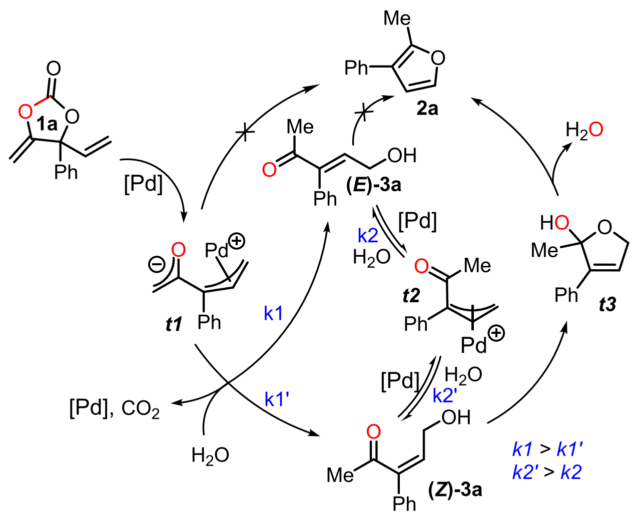
Scheme 3. Plausible Mechanism of the Water-Mediated Decarboxylation towards the Polysubstituted Furans and Allylic Alcohols[a]



[a]Ligand is omitted for clarity.

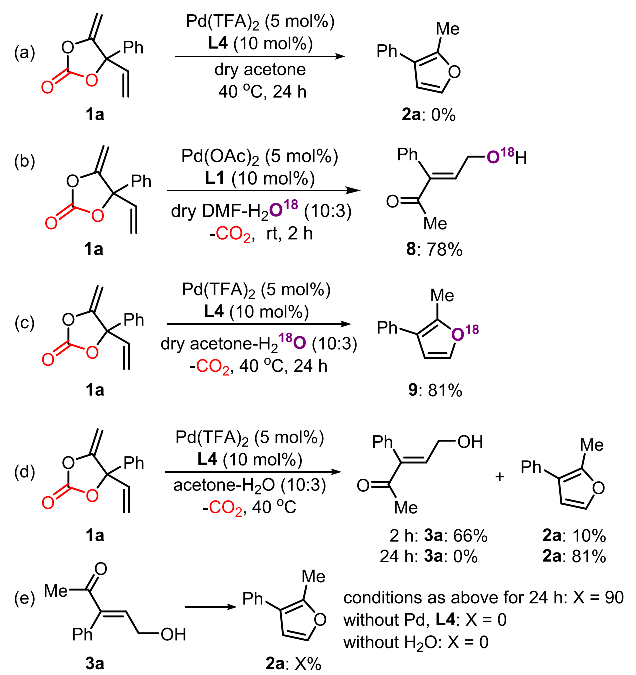


Figure 4. Control experiments using **1a** and **3a** as substrates under different conditions.

acetone-based solvent led to the formation of ^{18}O-labeled allylic alcohol **8** (Figure 4b) or furan **9** (Figure 4c) under the standard conditions in decent yields, suggesting the occurrence of the water nucleophilic attack. A substantial amount of the (*E*)-allylic alcohol **3a** (66% in yield) was isolated when the reaction toward the formation of furan was run for a shorter amount of time (2 vs 24 h, Figure 4d). Under the optimized conditions toward the formation of furan, the allylic alcohol **3a** could be easily converted into the furan **2a** in 90% isolated yield (Figure 4e); interestingly, no reaction occurred in the absence of palladium precatalyst or water while keeping other factors unchanged (Figure 4e). Taken our experimental observations and previous reports into consideration,[9a,b,10,12,13] a plausible mechanism was proposed as depicted in Scheme 3. The decarboxylation of the carbonate **1a** took place in the presence of suitable palladium precatalyst and ligand to generate a zwitterionic species ***t1***. The water nucleophilic attack of the intermediate ***t1*** would give rise to either allylic alcohol (*E*)-**3a** or (*Z*)-**3a** but with the formation of (*E*)-**3a** favored (k1 > k1′). The stereoisomer (*E*)-**3a** is stable and isolatable, while the corresponding (*Z*)-**3a** was readily converted to furan **2a** through ***t3*** upon an intramolecular nucleophilic attack followed by a dehydration process. The ratio of the stereoisomers (*E*)-**3a**/(*Z*)-**3a** could be controlled by judicious choice of the ligand and reaction conditions. In the presence of water and palladium catalyst, the interconversion of the stereoisomers of **3a** occurred through palladium allyl intermediate ***t2*** in which the dangling hydroxyl group acts as a leaving group with the water as nucleophile. In the current system, the water nucleophilic attack of ***t2*** toward the (*Z*)-**3a** is more favored (k2′ > k2) as suggested from the control experiments in Figure 4d.

In summary, we have developed an interesting water-mediated catalytic decarboxylation process toward the formation of polysubstituted furans and (*E*)-allylic alcohols. This protocol features wide functional group tolerance, easy operation, and only CO_2 byproduct generation. These reactions can be performed on gram scale open to air under extremely ambient conditions. A range of control experiments revealed the crucial role of the water for the successful conversions as well as the origin of the chemoselectivity and exclusive stereoselectivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00929.

Experimental details and characterization data (PDF)

Accession Codes

CCDC 2022999 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Wusheng Guo − *Frontier Institute of Science and Technology (FIST), Xi'an Jiaotong University, Xi'an 710045, China; Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, Xi'an Jiaotong University, Xi'an 710049, China;* orcid.org/0000-0001-5259-3600; Email: wusheng.guo@mail.xjtu.edu.cn

Authors

Yulian Yang − *School of Biology and Biological Engineering, South China University of Technology, Guangzhou 510006, China; Frontier Institute of Science and Technology (FIST), Xi'an Jiaotong University, Xi'an 710045, China*

Linhong Zuo − *Frontier Institute of Science and Technology (FIST), Xi'an Jiaotong University, Xi'an 710045, China*

Kun Wei − *School of Biology and Biological Engineering, South China University of Technology, Guangzhou 510006, China*

Complete contact information is available at:
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Author Contributions

[†]Y.Y. and L.Z. contributed equally.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Anastas, P. T.; Warner, J. *Green Chemistry Theory and Practice*; Oxford University Press: Oxford, 1998. (b) Anastas, P. T.; Kirchhoff, M. M. Origins, Current Status, and Future Challenges of Green Chemistry. *Acc. Chem. Res.* **2002**, *35*, 686−694.

(2) The use of water as nucleophile is challenging and under-developed. For selected examples, see: (a) Jacobsen, E. N. Asymmetric Catalysis of Epoxide Ring-Opening Reactions. *Acc. Chem. Res.* **2000**, *33*, 421−431. (b) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. Asymmetric Catalysis with Water: Efficient Kinetic Resolution of Terminal Epoxides by Means of Catalytic Hydrolysis. *Science* **1997**, *277*, 936−938. (c) Dong, G.; Teo, P.; Wickens, Z. K.; Grubbs, R. H. Primary Alcohols from Terminal Olefins: Formal Anti-Markovnikov Hydration via Triple Relay Catalysis. *Science* **2011**, *333*, 1609−1612. (d) Lee, M.; Sanford, M. S. Platinum-Catalyzed, Terminal-Selective C(sp^3)-H Oxidation of Aliphatic Amines. *J. Am. Chem. Soc.* **2015**, *137*, 12796−12799. (e) Kramer, S.; Madsen, J. L. H.; Rottländer, M.; Skrydstrup, T. Access to 2,5-Diamidopyrroles and 2,5-Diamidofurans by Au(I)-Catalyzed Double Hydroamination or Hydration of 1,3-Diynes. *Org. Lett.* **2010**, *12*, 2758−2761. (f) Khan, A.; Khan, S.; Khan, I.; Zhao, C.; Mao, Y.; Chen, Y.; Zhang, Y. J. Enantioselective Construction of Tertiary C-O Bond via Allylic Substitution of Vinylethylene Carbonates with Water and Alcohols. *J. Am. Chem. Soc.* **2017**, *139*, 10733−10741.

(3) (a) Boto, A.; Alvarez, L. In *Heterocycles in Natural Product Synthesis*; Majumdar, K. C., Chattopadhyay, S. K., Eds.; Wiley-VCH: Weinheim, 2011; p 99. (b) Brown, R. C. D. Developments in Furan Syntheses. *Angew. Chem., Int. Ed.* **2005**, *44*, 850−852. (c) Gidron, O.; Diskin-Posner, Y.; Bendikov, M. α-Oligofurans. *J. Am. Chem. Soc.* **2010**, *132*, 2148−2150.

(4) (a) Montagnon, T.; Tofi, M.; Vassilikogiannakis, G. Using Singlet Oxygen to Synthesize Polyoxygenated Natural Products from Furans. *Acc. Chem. Res.* **2008**, *41*, 1001−1011. (b) Teixeira, I. F.; Lo, B. T. W.; Kostetskyy, P.; Ye, L.; Tang, C. C.; Mpourmpakis, G.; Tsang, S. C. E. Direct Catalytic Conversion of Biomass-Derived Furan and Ethanol to Ethylbenzene. *ACS Catal.* **2018**, *8*, 1843−1850.

(5) For selected reviews, see: (a) Keay, B. A. Synthesis of Multi-Substituted Furan Rings: The Role of Silicon. *Chem. Soc. Rev.* **1999**, *28*, 209−215. (b) Kirsch, S. F. Syntheses of Polysubstituted Furans: Recent Developments. *Org. Biomol. Chem.* **2006**, *4*, 2076−2080. (c) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. Transition Metal-Mediated Synthesis of Monocyclic Aromatic Heterocycles. *Chem. Rev.* **2013**, *113*, 3084−3213.

(6) For selected examples, see: (a) Dudnik, A. S.; Xia, Y.; Li, Y.; Gevorgyan, V. Computation-Guided Development of Au-Catalyzed Cycloisomerizations Proceeding via 1,2-Si or 1,2-H Migrations: Regiodivergent Synthesis of Silylfurans. *J. Am. Chem. Soc.* **2010**, *132*, 7645−7655. (b) El Arba, M.; Dibrell, S. E.; Meece, F.; Frantz, D. E. Ru (II)-Catalyzed Synthesis of Substituted Furans and Their Conversion to Butenolides. *Org. Lett.* **2018**, *20*, 5886−5888.

(7) For selected examples, see: (a) Cui, X.; Xu, X.; Wojtas, L.; Kim, M. M.; Zhang, X. P. Regioselective Synthesis of Multisubstituted Furans via Metalloradical Cyclization of Alkynes with α-Diazocarbonyls: Construction of Functionalized α-Oligofurans. *J. Am. Chem. Soc.* **2012**, *134*, 19981−19984. (b) Wu, J.; Yoshikai, N. Modular Synthesis of Multisubstituted Furans through Palladium Catalyzed Three-Component Condensation of Alkynylbenziodoxoles, Carboxylic Acids, and Imines. *Angew. Chem., Int. Ed.* **2015**, *54*, 11107−11111. (c) Lad, B. S.; Katukojvala, S. Piano-Stool Rhodium Enalcarbenoids: Application to CatalystControlled Metal-Templated Annulations of Diazoenals and 1,3- Dicarbonyls. *ACS Catal.* **2018**, *8*, 11807−11814.

(8) For selected examples, see: (a) Jung, C. K.; Wang, J. C.; Krische, M. J. Phosphine-Mediated Reductive Condensation of γ-Acyloxy Butynoates: A Diversity Oriented Strategy for the Construction of Substituted Furans. *J. Am. Chem. Soc.* **2004**, *126*, 4118−4119. (b) Albrecht, Ł.; Ransborg, L.; Gschwend, K. B.; Jørgensen, K. A. An Organocatalytic Approach to 2-Hydroxyalkyl- and 2-Aminoalkyl Furanes. *J. Am. Chem. Soc.* **2010**, *132*, 17886−17893.

(9) For a review, see: (a) Guo, W.; Gómez, E.; Cristofol, A.; Xie, J.; Kleij, A. W. Catalytic Transformations of Functionalized Cyclic Organic Carbonates. *Angew. Chem., Int. Ed.* **2018**, *57*, 13735−13747. (b) Zuo, L.; Liu, T.; Chang, X.; Guo, W. An Update of Transition Metal-Catalyzed Decarboxylative Transformations of Cyclic Carbonates and Carbamates. *Molecules* **2019**, *24*, 3930−3946. (c) Wei, Y.; Hu, P.; Zhang, M.; Su, W. Metal-Catalyzed Decarboxylative C-H Functionalization. *Chem. Rev.* **2017**, *117*, 8864−8907. (d) Rodríguez, N.; Goossen, L. J. Decarboxylative Coupling Reactions: A Modern Strategy for C-C-Bond Formation. *Chem. Soc. Rev.* **2011**, *40*, 5030−5048. (e) De, N.; Yoo, E. J. Recent Advances in the Catalytic Cycloaddition of 1, n-Dipoles. *ACS Catal.* **2018**, *8*, 48−58. (f) Li, T. R.; Wang, Y. N.; Xiao, W. J.; Lu, L. Q. Transition-Metal-Catalyzed Cyclization Reactions using Vinyl and Ethynyl Benzoxazinones as Dipole Precursors. *Tetrahedron Lett.* **2018**, *59*, 1521−1530. For selected research articles, see: (g) Ohmatsu, K.; Imagawa, N.; Ooi, T. Ligand-Enabled Multiple Absolute Stereocontrol in Metal-catalysed Cycloaddition for Construction of Contiguous All-Carbon Quaternary Stereocentres. *Nat. Chem.* **2014**, *6*, 47−51. (h) Yang, L. C.; Wang, Y. N.; Liu, R.; Luo, Y.; Ng, X. Q.; Yang, B.; Rong, Z.-Q.; Lan, Y.; Shao, Z.; Zhao, Y. Stereoselective Access to [5.5.0] and [4.4.1] Bicyclic Compounds through Pd-Catalysed Divergent Higher-Order Cycloadditions. *Nat. Chem.* **2020**, *12*, 860−868. (i) Komatsuki, K.; Sadamitsu, Y.; Sekine, K.; Saito, K. Yamada, T. Stereospecific Decarboxylative Nazarov Cyclization Mediated by Carbon Dioxide for the Preparation of Highly Substituted 2-Cyclopentenones. *Angew. Chem., Int. Ed.* **2017**, *56*, 11594−11598. (j) Komatsuki, K.; Kozuma, A.; Saito, K.; Yamada, T. Decarboxylative Nazarov Cyclization-Based Chirality Transfer for Asymmetric Synthesis of 2-Cyclopentenones. *Org. Lett.* **2019**, *21*, 6628−6632.

(10) Guo, W.; Martínez-Rodríguez, L.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Highly Efficient Catalytic Formation of (*Z*)-1,4-But-2-ene Diols Using Water as a Nucleophile. *Angew. Chem., Int. Ed.* **2016**, *55*, 11037−11040.

(11) Flynn, A. B.; Ogilvie, W. W. Stereocontrolled Synthesis of Tetrasubstituted Olefins. *Chem. Rev.* **2007**, *107*, 4698−4745.

(12) (a) Yan, B. W.; Zuo, L.; Chang, X.; Liu, T.; Cui, M.; Liu, Y.; Sun, H.; Dang, L.; Guo, W. Kinetically Controllable Pd-Catalyzed Decarboxylation Enabled [5 + 2] and [3 + 2] Cycloaddition toward Carbocycles Featuring Quaternary Carbons. *Org. Lett.* **2021**, *23*, 351−357. (b) Zuo, L.; Yang, Y.; Guo, W. Modular Domino Process toward Highly Functionalized Pyrroles via Pd-Catalyzed [4 + 1] Annulation under Mild Conditions. *Org. Lett.* **2021**, *23*, 2013−2018.

(13) For selected reviews, see: (a) Lumbroso, A.; Cooke, M. L.; Breit, B. Catalytic Asymmetric Synthesis of Allylic Alcohols and Derivatives and their Applications in Organic Synthesis. *Angew. Chem., Int. Ed.* **2013**, *52*, 1890−1932. (b) Sundararaju, B.; Achard, M.; Bruneau, C. Transition Metal Catalyzed Nucleophilic Allylic

Substitution: Activation of Allylic Alcohols via π-Allylic Species. *Chem. Soc. Rev.* **2012**, *41*, 4467−4483.

(14) (a) Li, D. R.; Murugan, A.; Falck, J. R. Enantioselective, Organocatalytic Oxy-Michael Addition to γ/δ-Hydroxy-α, β-enones: Boronate-Amine Complexes as Chiral Hydroxide Synthons. *J. Am. Chem. Soc.* **2008**, *130*, 46−48. (b) Nicolaou, K. C.; Lim, Y. H.; Becker, J. Total Synthesis and Absolute Configuration of the Bisanthraquinone Antibiotic BE-43472B†. *Angew. Chem., Int. Ed.* **2009**, *48*, 3444−3448. (c) Hutchings-Goetz, L.; Yang, C.; Snaddon, T. N. Enantioselective α-Allylation of Aryl Acetic Acid Esters via C1-Ammonium Enolate Nucleophiles: Identification of a Broadly Effective Palladium Catalyst for Electron-Deficient Electrophiles. *ACS Catal.* **2018**, *8*, 10537−10544.

(15) For synthetic details of the carbonate substrates, see ref 12.

(16) (a) Yang, X.; Wu, T.; Phipps, R. J.; Toste, F. D. Advances in Catalytic Enantioselective Fluorination, Mono-, Di-, and Trifluoromethylation, and Trifluoromethylthiolation Reactions. *Chem. Rev.* **2015**, *115*, 826−870. (b) Zhu, Y.; Han, J. L.; Wang, J. D.; Shibata, N.; Sodeoka, M.; Soloshonok, V. A.; Coelho, J. A. S.; Toste, F. D. Modern Approaches for Asymmetric Construction of Carbon-Fluorine Quaternary Stereogenic Centers: Synthetic Challenges and Pharmaceutical Needs. *Chem. Rev.* **2018**, *118*, 3887−3964.

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