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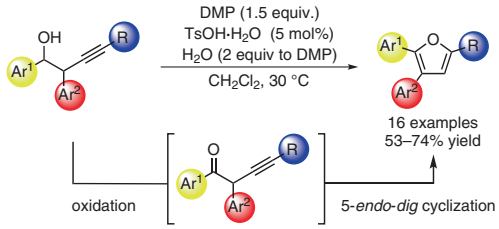
Dess–Martin Periodinane/Brønsted Acid-Mediated Tandem Oxidation/Cyclization of Homopropargylic Alcohols for Synthesis of Trisubstituted Furans

Miki Murakami[a]
Megumi Miyazaki[b]
Mayo Ishibashi[c]
Mizuki Oda[b]
Karin Takekuma[b]
Yoshikazu Horino*[b]

[a] Graduate School of Innovative Life Science, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan
[b] Department of Applied Chemistry and Bioscience, Chitose Institute of Science and Technology, Bibi 65-758, Chitose, Hokkaido 066-8655, Japan
y-horino@photon.chitose.ac.jp
[c] Graduate School of Science and Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan



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Abstract A facile, efficient, and metal-free single-flask procedure for the synthesis of trisubstituted furans from simple readily available homopropargylic alcohols is described. A combination of Dess–Martin periodinane, H_2O, and TsOH·H_2O plays a crucial role in the formation of the trisubstituted furans. The advantages of this method include operational ease, mild reaction conditions, and good functional-group tolerance.

Key words furans, Dess–Martin oxidation, 5-*endo-dig* cyclization, Brønsted acids, homopropargylic alcohols

The furan scaffold is well documented to be present in pharmaceuticals,[1] bioactive natural products,[2] and polymers.[3] Moreover, furans are widely recognized to serve as valuable synthetic building blocks for constructing more-advanced motifs in organic synthesis;[4] consequently, numerous methods have been developed for their synthesis.[5] The Feist–Bénary synthesis[6] and the Paal–Knorr condensation[7] are the most frequently used furan-synthesis methods, and many effective approaches for synthesizing functionalized furans have been developed since these methods were first reported. Most existing catalytic furan-synthesis systems involve a cycloisomerization/cyclization strategy based on alkynes or allenes with activation by metals such as Pd(II),[8] Cu(I/II),[9] Zn,[10] Ag (I),[8l,11] Au(I/III),[8l,12] Rh(I/II),[8l,13] Cr(0), W(0), Ru(II), or Pt(II)[8l,14] (Scheme 1a). Compared with well-established transition-metal-catalyzed approaches, transition-metal-free furan syntheses aimed at promoting an intramolecular cyclization event are less well explored. For example, Chong and co-workers reported that the cyclization of β-alkynylated ketones in the presence of 50 mol% of oxalic acid afforded substituted furans (Scheme 1b).[15] Unfortunately, the poor functional-group tolerance of methods used to synthesize β-alkynylated ketones hinder efficient access to functionalized furans. Liu and co-workers demonstrated a 2-iodoxybenzoic acid (IBX)-mediated synthesis of 3,5-substituted 2-acylfurans from (*Z*)-alkynylated allylic alcohols by using a tandem oxidation/cyclization process (Scheme 1c),[16] and base-promoted oxacyclizations of (*Z*)-alkynylated-allylic alcohols have also recently been reported to afford polysubstituted furans;[17] however, these methods require the synthesis of geometrically defined (*Z*)-alkene substrates. On the other hand, electrophilic cyclizations of homopropargylic ketones or 4-dimethoxyphosphoryl-substituted allenyl alcohols promoted by a stoichiometric amount of NBS, NIS,[18] I_2,[19] or a Brønsted acid[20] afford the corresponding tri- or tetrasubstituted furans (Scheme 1d). Although cycloisomerization and cyclization strategies provide noteworthy results, it should be noted that methods for constructing highly functionalized furans normally involve difficult preparations of precursors. Therefore, devising synthetic strategies that provide access to substituted furans under mild conditions from simple and readily available starting materials remains an important objective.

We recently reported the practical syntheses of highly functionalized homopropargylic alcohols from readily accessible propargylic acetates.[21] In the course of this study, we noted that the Dess–Martin periodinane (DMP) oxidation[22] of homopropargylic alcohols occasionally led to the selective formation of 2,3,5-trisubstituted furans under mild reaction conditions, with old DMP providing better re-

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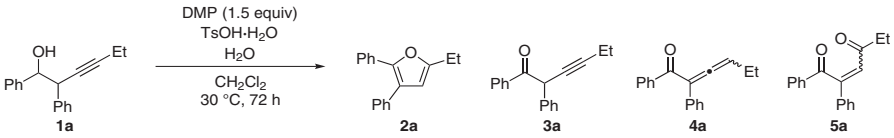
Table 1 Optimizing the Reaction Conditions[a]



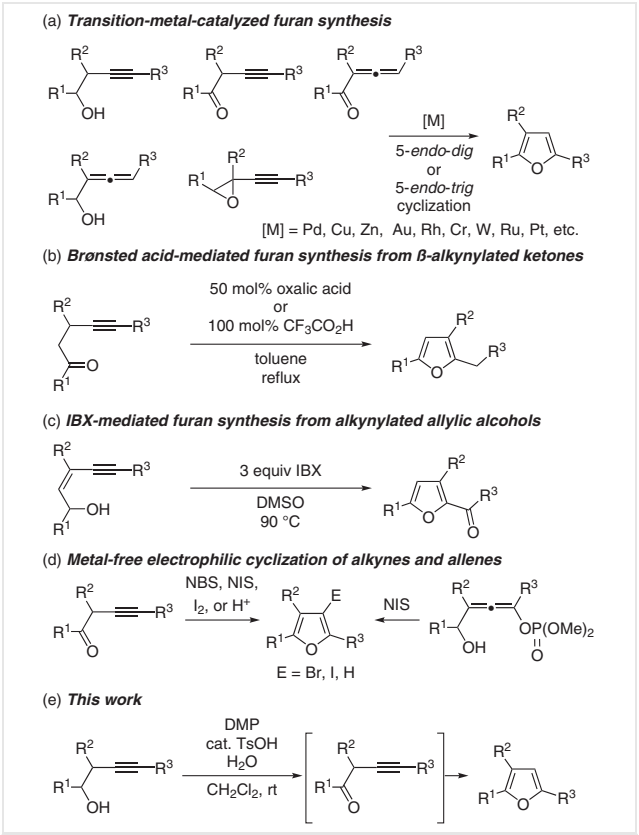
Entry	H_2O (equiv to DMP)	TsOH·H_2O (mol%)	Yield[b] (%)			
			2a	**3a**[b]	**4a**	**5a**
1	–	–	31	trace	trace	5
2[c]	–	–	0	74	0	0
3	1	–	6	42	13	0
4	1	5	41	11	2	trace
5	1.5	5	46	3	2	2
6	2	5	63	0	0	2
7	3	5	46	12	7	trace
8	4	5	53	0	0	0
9[d]	2	5	53	8	4	0
10[e]	2	5	63	0	0	0
11[f]	2	10	49	4	5	0
12[f]	2	20	8	17	7	0

[a] Reaction conditions: **1a** (0.3 mmol), DMP (0.45 mmol), H_2O, TsOH·H_2O, anhyd CH_2Cl_2, 30 °C, 72 h.
[b] Isolated yields.
[c] 0.5 h reaction time.
[d] 48 h reaction time.
[e] 60 h reaction time.
[f] 24 h reaction time.

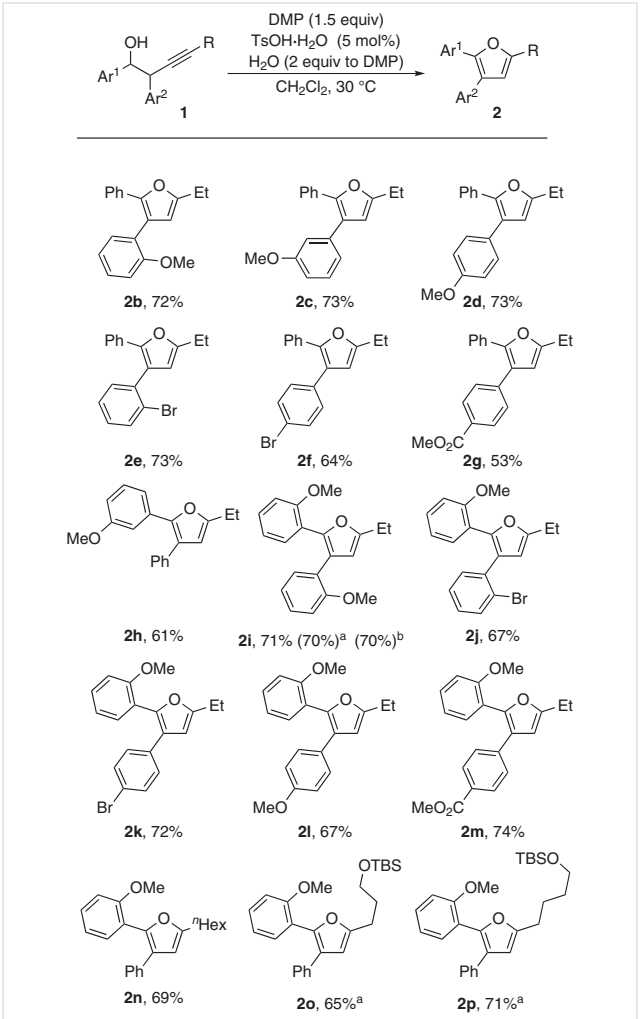
sults than fresh DMP. As part of our explorations to derive reliable and more-efficient transition-metal-free furan syntheses and to provide deeper insights into the reaction mechanisms, we describe the successful development of a DMP/Brønsted acid-promoted tandem oxidation/cyclization reaction for the preparation of 2,3,5-trisubstituted furans from homopropargylic alcohols that is both efficient and functional-group-tolerant (Scheme 1e). To the best of our knowledge, no attention has previously been paid to homopropargylic alcohols as building blocks for 2,3,5-trisubstituted furans under transition-metal-free conditions, despite these reactants being more readily accessible and more easily manipulated than previously reported precursors.

Our initial investigation focused on the DMP/Brønsted acid-promoted tandem oxidation/cyclization reaction of the homopropargylic alcohol **1a** (Table 1).[23] Whereas the DMP oxidation of **1a** gave ketone **3a** in 74% yield, a prolonged reaction time afforded the 2,3,5-trisubstituted furan **2a** in 31% yield along with diketone **5a** (Table 1, entries 1 and 2). The formation of **5a** is possibly ascribable to the oxidative ring opening of **2a**.[24] As a prolonged reaction time led to the decomposition of both **2a** and **3a**, we next explored decreasing the reactivity of DMP by the addition of H_2O.[22c] Although 1.0 equivalents of H_2O gave **2a** in 6% yield, to our delight, the single-flask procedure for the synthesis of the trisubstituted furan was accelerated dramatically when a catalytic amount of *p*-toluenesulfonic acid monohydrate (TsOH·H_2O) was added, which afforded **2a** in 41% yield (entries 3 and 4). Among the loadings of H_2O examined, the use of 2.0 equivalents (relative to DMP) produced the best result, giving **2a** in 63% yield (entries 4–8). Note that reproducible outcomes were difficult to achieve when less than 2.0 equivalents of H_2O were used (entries 4 and 5). Reducing the reaction time was found to suppress the formation of **5a** (entries 6, 9, and 10). In addition, higher amounts of TsOH·H_2O did not affect the efficiency of this reaction (entries 11 and 12).

With the optimized reaction conditions in hand, we examined the scope of our DMP/Brønsted acid-promoted tandem oxidation/cyclization reaction for the production of trisubstituted furans **2** (Scheme 2). The method efficiently produced trisubstituted furans bearing a variety of electronically diverse substituents. For example, trisubstituted furans **2b–g** were produced irrespective of the electronic nature of the substituent on the propargylic benzene ring (Ar^2).



Scheme 1 Synthesis of furans from homopropargylic alcohols and their derivatives

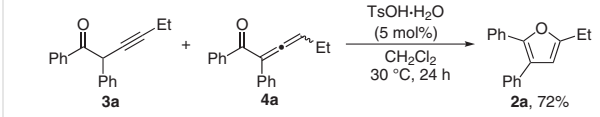


Scheme 2 Substrate scope. *Reaction conditions*: **1** (0.3 mmol), DMP (0.45 mmol), H_2O (2 equiv relative to DMP), $TsOH·H_2O$ (5 mol%), anhyd CH_2Cl_2. [a] The reaction was carried out for 60 h in the absence of $TsOH·H_2O$. [b] **1i** (3.0 mmol) was used.

We next evaluated the influence of the homopropargylic substituent (Ar^1). Whereas the reaction of the 3-methoxy-substituted substrate gave **2h** in 61% yield, substrates bearing a 2-methoxyphenyl group at the homopropargylic position reacted efficiently even in the absence of $TsOH·H_2O$, albeit with prolonged reaction times. Indeed, whereas the reaction of **1i** with $TsOH·H_2O$ required 36 hours to afford **2i** in 71% yield, 60 h were required in the absence of $TsOH·H_2O$ to give **2i** in 70% yield. Moreover, **1i** provided **2i** in 70% yield in a 3 mmol-scale reaction.

We next examined the effect of the substituent (R) adjacent to the alkyne moiety. Replacing the ethyl group with hexyl group afforded the corresponding product **2n** in comparable yield under otherwise identical reaction conditions. In addition, as we had found that **2i** could be prepared without the assistance of $TsOH·H_2O$, we subjected TBSO-substituted substrates **1o** and **1p** to the furan-synthesis procedure in the absence of $TsOH·H_2O$; these reactions successfully afforded **2o** and **2p**, respectively, with the Si–O bond remaining intact.

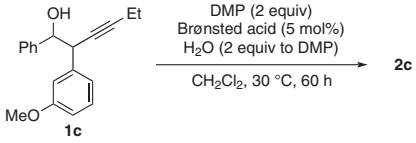
To determine whether or not the Brønsted acid-mediated intramolecular cyclization of a homopropargylic ketone proceeds in a catalytic manner, we exposed a mixture of **3a** and **4a** to a catalytic amount of $TsOH·H_2O$ (Scheme 3). As expected, the Brønsted acid-catalyzed intramolecular cyclization gave **2a** in 72% isolated yield, which suggests that $TsOH·H_2O$ functions as a Brønsted acid that promotes cyclization. Accordingly, an alternative pathway involving a hypervalent iodine species that promotes the cycloisomerization of **3a** and **4a** to give **2a** can be ruled out, because such a system would require excess IBX.[16] It is worth noting that the Brønsted acid-catalyzed synthesis of a furan from an α-alkynylated ketone appears to be unprecedented.



Scheme 3 TsOH-catalyzed furan synthesis from a mixture of **3a** and **4a**

We next evaluated the effect of the Brønsted acid (Table 2). Among the sulfonic acids examined, TsOH·H_2O proved to be ideal for forming trisubstituted furans in a single-flask procedure. For example, **2c** was obtained in 73% yield when the reaction was performed in the presence of DMP and a catalytic amount of TsOH·H_2O (Table 1, entry 1). Conversely, a significantly lower yield of **2c** was observed when $MeSO_3H$, CF_3SO_3H, or 10-camphorsulfonic acid (10-CSA) was used instead of TsOH·H_2O (entries 2–4).

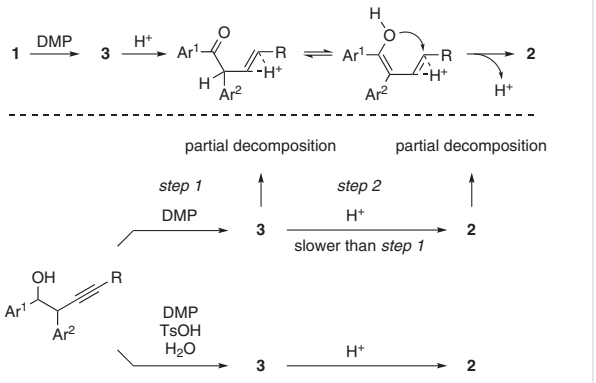
Table 2 Effect of the Brønsted Acid[a]



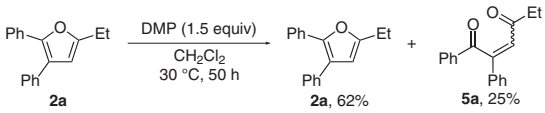
entry	Brønsted acid	Yield[b] (%) of **2c**
1	TsOH·H_2O	73
2	$MeSO_3H$	11
3	CF_3SO_3H	11
4	10-CSA	20

[a] Reaction conditions: **1c** (0.3 mmol), DMP (0.45 mmol), H_2O (2 equiv relative to DMP), Brønsted acid (5 mol%), anhyd CH_2Cl_2, 30 °C, 60 h.
[b] Isolated yield.

We propose that the reaction proceeds through the activation of both the alkyne and ketone by TsOH, followed by intramolecular cyclization (Scheme 4). The water present in the reaction mixture partially deactivates the DMP, with the homopropargyl ketone and furan partially decomposing in the absence of water. In fact, we observed that **2a** partially decomposes under DMP-oxidation conditions (Scheme 5). On the other hand, whereas the addition of water leads to slower alcohol oxidation, the decomposition of **2** and **3** is also inhibited due to the lower activity of the DMP and the lower concentration of the homopropargylic ketone **3**. Additionally, the decomposition of furan **2** is also restrained. Together, these effects are believed to be responsible for the efficient syntheses of trisubstituted furans.



Scheme 4 Plausible reaction pathway



Scheme 5 Oxidative ring-opening reaction of **2a**

In conclusion, we have developed a facile, efficient, and metal-free single-flask procedure for synthesizing 2,3,5-trisubstituted furans from easily accessible homopropargylic alcohols. The reaction proceeds through alcohol oxidation followed by a 5-*endo-dig* cyclization, in which the added H_2O and TsOH·H_2O play crucial roles.

Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-2047-9765.

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(23) **5-Ethyl-3-(2-methoxyphenyl)-2-phenylfuran (2b); Typical Procedure**

Homopropargylic alcohol **1b** (0.3 mmol) and $TsOH·H_2O$ (5 mol%) were dissolved in anhyd CH_2Cl_2 (3 mL) under argon in a 10 mL vial equipped with a magnetic stirrer bar and a septum. Distilled H_2O (0.9 mmol) and Dess–Martin periodinane (0.6 mmol) were successively added to the stirred solution at ambient temperature. The septum was replaced with a screw cap under argon, and the resulting mixture (0.1 M) was stirred in an oil bath at 30 °C for 60 h until the reaction was complete (TLC). The reaction was quenched with sat. aq $NaHCO_3$ (1 mL) and $Na_2S_2O_3$ (1 mL), and the resulting mixture was stirred for 30 min. The separated aqueous layer was extracted with $CHCl_3$, and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The resulting crude residue was purified by flash chromatography (silica gel) to give a colorless oil; yield: 60.1 mg (72%), R_f = 0.59 (EtOAc–hexane, 3:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 1.2, 8.4 Hz, 2 H), 7.41–7.28 (m, 4 H), 7.22 (tt, *J* = 1.2, 7.6 Hz, 1 H), 7.03 (d, *J* = 7.2 Hz, 2 H), 6.20 (t, *J* = 1.2 Hz, 1 H), 3.77 (s, 3 H), 2.83 (dq, *J* = 1.2, 7.2 Hz, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 156.5, 147.4, 132.1, 131.5, 128.8, 128.2, 126.7, 125.3, 123.9, 120.8, 119.0, 111.3, 109.6, 55.5, 21.6, 12.2. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{19}H_{19}O_2$: 279.1385; found: 279.1391.

(24) For selected examples of oxidative ring-opening reaction of furans see: (a) Piancatelli, G.; Scettri, A.; D'Auria, M. *Tetrahedron* **1980**, *36*, 661. (b) Yadav, J. S.; Krishna, P. R.; Gurjar, M. K. *Tetrahedron* **1989**, *45*, 6263. (c) Kobayashi, Y.; Nakano, M.; Kumar, G. B.; Kishihara, K. *J. Org. Chem.* **1998**, *63*, 7505; see also ref. 4a.