

# Metal-Free Electrocatalytic Aerobic Hydroxylation of Arylboronic Acids

Jian Luo, Bo Hu, Alyssa Sam, and T. Leo Liu\*®

The Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322, United States

# **Supporting Information**

**ABSTRACT:** Hydroxylation of arylboronic acids to aryl alcohols was realized by a scalable electrocatalytic method. The present electrochemical hydroxylation employs low-cost methyl viologen as an organic cathodic electrocatalyst and involves  $O_2$  as a green and sustainable reactant. The electrochemical kinetic studies shown here can be a powerful tool to gain rich mechanistic and kinetic information and thus an in-depth understanding of the electrocatalytic mechanism.



lectrocatalysis constitutes a powerful, versatile, and environmentally benign protocol that has been intensively applied in the field of energy conversion, such as hydrogen evolution, water oxidation, and carbon dioxide reduction, in the last decades.<sup>1</sup> However, applications of electrocatalysis in organic synthesis have been largely underdeveloped, although early pioneering studies demonstrated the applicability of electrochemical synthesis.<sup>2</sup> Until recently, electrochemical or electrocatalytic organic synthesis has been advocated as a promising approach for scalable and sustainable chemical transformations that can be applied in chemical industries for the following reasons.<sup>3</sup> First, dangerous and toxic redox reagents are replaced by electric current and less toxic reaction waste, and byproducts are generated in the electrochemical process.<sup>3c,4</sup> Second, the redox control of a reaction can be facilely achieved by the voltage of electrodes, and then, better selectivity could be obtained than under the thermal reaction conditions.<sup>3a,b</sup> Third, a wide range of functional groups were tolerant to mild electrochemical conditions.<sup>2a,3b,4c</sup> Finally, the electrochemical approach can supply higher energy efficiency as compared to thermal and photochemical processes.<sup>4a,5</sup>

In noncatalytic electrochemical reactions, a heterogeneous electron transfer between the substrate and the electrode is the key step to generate reactive intermediates, followed by a series of homogeneous chemical transformations to produce final products.<sup>3a,6</sup> To accelerate the electron transfer while avoiding the over-oxidation/over-reduction of the substrates, and to mitigate the passivation of the electrode, electron-transfer mediators were commonly applied as electrocatalysts in electrosynthesis,<sup>3a,4c,7</sup> including *N*-oxyl radicals,<sup>3b,4c,d,7a</sup> triarylamines,<sup>7b</sup> triarylimidazoles,<sup>7c</sup> and ferrocene.<sup>7d</sup>

Our group has applied methyl viologen  $(MV^{2^+})$  and its derivatives for redox flow battery applications.<sup>8</sup> The redox active  $MV^{2^+}$  cation undergoes a reversible single-electron reduction at -0.45 V (vs NHE, in aqueous solution) corresponding to the  $MV^{2^+/^{\bullet+}}$  couple. Meanwhile, both redox states were extremely thermally stable. Hence,  $MV^{2^+}$  with its reversible and fast electron transfer can be a good candidate as an electron-transfer mediator for the electrocatalytic organic synthesis. Notably,  $\mathbf{MV}^{2+}$  containing salts can be easily prepared from commercially available chemicals at low cost (\$1.0/kg for  $\mathbf{MVCl}_2$ , \$8.8/kg for  $\mathbf{MV}(\mathbf{PF}_6)_2$ , see the Supporting Information (SI) for details). In the literature, there are very few examples of using  $\mathbf{MV}^{2+}$  as a catalyst for electrochemical synthesis.<sup>9</sup> In addition, we noticed that the one-electron-reduced  $\mathbf{MV}^{\bullet+}$  cation radical is highly air sensitive. Further literature research revealed that  $\mathbf{MV}^{\bullet+}$  can reduce O<sub>2</sub> to the superoxide,  $O_2^{\bullet-}$ , and then goes back to its original  $\mathbf{MV}^{2+}$  state.<sup>10</sup> This chemistry inspired us to apply  $O_2^{\bullet-}$  as an activated  $O_2$  reactant in organic reactions through electrocatalysis.<sup>11</sup>  $O_2^{\bullet-}$  is a highly active species that is widely involved in organic transformations, such as the oxidation of amines and alcohols.<sup>11,12</sup>

The phenolic hydroxyl is an important functional group that is widely present in drug molecules and natural products. There are traditional thermal reactions that have been developed to convert arylboronic acids into aryl alcohols.<sup>13</sup> However, among these methods either strong oxidants were needed<sup>13e,g</sup> or transition metals were used.<sup>13c,d</sup> Recent studies reported that photolytically generated  $O_2^{\bullet-}$  is highly reactive with arylboronic acids to produce corresponding aromatic alcohols.<sup>13a,b</sup> However, the photocatalysis entailed expensive photocatalysts and is not feasible to scale up. Herein, we demonstrate  $MV(PF_6)_2$  as a highly efficient and inexpensive organic cathodic electrocatalyst for scalable electrochemical aerobic hydroxylation of arylboronic acids to aryl alcohols involving O<sub>2</sub> in air as a green reactant. In contrast, many reported electrocatalytic synthesis are triggered by an anodic electrocatalyst.<sup>3a,4c,7</sup> In addition, in the literature, the utilization of electrochemical analysis for mechanistic understanding has been largely overlooked by synthetic chemists. Electrochemical mechanistic and kinetic studies were conducted to gain an indepth understanding on the reaction catalyzed by the MV(PF<sub>6</sub>)<sub>2</sub> electrocatalyst. In particular, an arylboronic acid-O<sub>2</sub> adduct, instead of O<sub>2</sub>, was detected as the actual substrate

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undergoing electrochemical reduction by  $\mathbf{MV}^{\bullet+}\!\!\!,$  the actived catalyst.

The electrochemical study was first conducted on the  $MV^{2+}/O_2$ /phenylboronic acid (PhB(OH)<sub>2</sub>) system. As shown in Figure 1, O<sub>2</sub> displayed a reversible one-electron reduction peak



Figure 1. CV curves of (a)  $O_2$ -saturated DMF, (b) 0.1 M PhB(OH)<sub>2</sub> in  $O_2$ -saturated DMF, (c) 2.5 mM **MV**(**PF**<sub>6</sub>)<sub>2</sub> under  $N_{2'}$  (d) 2.5 mM **MV**(**PF**<sub>6</sub>)<sub>2</sub> with 0.1 M PhB(OH)<sub>2</sub> under  $N_{2'}$  (e) 2.5 mM **MV**(**PF**<sub>6</sub>)<sub>2</sub> under  $O_2$ , and (f) 2.5 mM **MV**(**PF**<sub>6</sub>)<sub>2</sub> with 0.1 M PhB(OH)<sub>2</sub> under  $O_2$ . All tests were conducted in DMF solution with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. Working electrode: glassy carbon, counter electrode: carbon rod, reference electrode: Ag/Ag<sup>+</sup>, scan rate: 100 mV/s. All potential was versus ferrocenium/ferrocene (Cp<sub>2</sub>Fe<sup>+/0</sup>).

with  $E_{1/2} [O_2^{0/\bullet}] = -1.32 \text{ V}$  (vs  $Cp_2Fe^{+/0}$ ) (Figure 1a) and became irreversible in the presence of PhB(OH)<sub>2</sub> (Figure 1b). It is because the superoxide radical anion  $(O_2^{\bullet-})$  was trapped by the PhB(OH)<sub>2</sub>, and then the return peak disappeared.  $MV^{2+}$ showed a reversible redox signal with  $E_{1/2} [\mathbf{MV}^{2+/\bullet+}] = -0.94 \text{ V}$ under  $N_2$  atmosphere (Figure 1c), and it remains unchanged in the presence of  $PhB(OH)_2$  (Figure 1d). Under an  $O_2$ atmosphere, the peak current intensity of the reduction process  $(MV^{2^{\hat{+}}} \rightarrow MV^{\hat{\bullet}+})$  was slightly increased and that of the oxidation process  $(MV^{\bullet+} \rightarrow MV^{2+})$  was slightly decreased (Figure 1e and Figure S2). We believe there is an electrontransfer equilibrium:  $\mathbf{MV}^{\bullet+} + \mathbf{O}_2 \leftrightarrow \mathbf{MV}^{2+} + \mathbf{O}_2^{\bullet-}$  (eq 1), and the electron-transfer equilibrium resides on the side of  $\mathbf{MV}^{\bullet+}$  because of the less negative  $E_{1/2} [\mathbf{MV}^{2+/\bullet+}]$  compared to  $E_{1/2}$  $[O_2^{0/\bullet-}]$ . However, in the presence of both PhB(OH)<sub>2</sub> and O<sub>2</sub>, an obvious electrocatalytic current was observed with  $E_{1/2}$  = -0.92 V, and the return peak completely disappeared (Figure 1f). It was interpreted that the reduced  $O_2$  was trapped by the  $PhB(OH)_2$ , and then, the chemical equilibrium eq 1 was shifted to the  $MV^{2+}$  side. Comparing the CV curves a-f, the reductive potential of  $O_2^{0/\bullet-}$  was reduced by 0.4 V in the presence of  $MV^{2+}$ . Meanwhile, in the presence of O<sub>2</sub> and PhB(OH)<sub>2</sub>, the peak current intensity of  $\mathbf{MV}^{2+}$  reduction was increased about 5 times (Figure 1c,f), which indicates that  $MV^{2+}$  is an efficient catalyst for the reduction of molecule O<sub>2</sub>.

On the basis of the above half-cell results, potentiostatic electrolysis experiments in a full cell were conducted to investigate the synthetic effectiveness of the electrocatalytic aerobic hydroxylation of arylboronic acids. After systematic optimization of reaction conditions (see Table S1), a 10 mL solution of 0.1 M 4-formylphenylboronic acid and 0.3 M Et<sub>3</sub>N, 0.01 M **MV**(**PF**<sub>6</sub>)<sub>2</sub> in DMF with 0.1 M Bu<sub>4</sub>N(**PF**<sub>6</sub>) as supporting electrolyte was electrolyzed in an undivided cell at -1.0 V (vs Cp<sub>2</sub>Fe<sup>+/0</sup>) in air using the chronocoulometry (CC) method with porous carbon as an anode and cathode and Ag/ Ag<sup>+</sup> electrode as a reference (see the picture in the SI). Et<sub>3</sub>N acts as a hydrogen atom donor. After the starting material was consumed, 4-hydroxybenzaldehyde was isolated as the main product with 87% yield and 66% faradic efficiency (FE) (Table 1, entry 1). In addition, control experiments confirmed the

 Table 1. Substrate Scope of the Electrocatalytic Aerobic

 Hydroxylation of Arylboronic Acids<sup>a</sup>

A	$\begin{array}{c} \text{MV(PF_6)}_2 (10 \text{ mol \%}) \\ \text{Et}_3 N (3.0 \text{ equiv}) \\ \hline \text{Bu}_4 N(\text{PF}_6) (0.1 \text{ M}) \\ \hline \text{DMF, air, rt} \\ \text{undivided cell} \\ -1.0 \text{ V (vs } \text{Cp}_2 \text{Fe}^{+/0}) \end{array} Ar - \text{OH}$						
substrates	yield, %	FE,⊓%			substrates	yield, %	FE, %
°	87 90	70 71 <sup>ь</sup>		7	NC-	92	76
Br-	92	70		8		82	58
	79 66	71 62°		9	EtO-	68	52
	84	62		10	MeO-	59	51
$\langle \rangle$	77	56		11	Ĵ	89	62
o≡t				12	$\bigcirc - \bigcirc +$	82	60
	86	64		13	C→B <sup>O</sup> C↓	62	54

 $^{a}$ 1.0 mmol scale reaction.  $^{b}$ 5.0 g scale reaction.  $^{c}$ 50 g scale reaction.  $^{d}$ FE stands for faradaic efficiency.

necessity of  $MV^{2+}$ , Et<sub>3</sub>N, electrolysis, and an O<sub>2</sub> atmosphere (Table S2, entries 2–7). When 2.0 equiv of benzoquinone (BQ) was added into the reaction mixture to quench radical intermediates (Table S2, entry 8), no product was found. The observation indicated a radical reaction mechanism for this reaction, which is consistent with the photocatalytic approaches.<sup>13a,b</sup>

The  $MV^{2+}/O_2/arylboronic acid electrocatalytic system was$ further applied to a wide scope of substrates. As shown in Table1, moderate to high yields (59–92%) were obtained withsatisfactory faradic efficiency (51–76%) for all the aryl alcoholsfrom the corresponding substrates. In the case of PhB(OH)<sub>2</sub>,79% isolated yield and 71% faradic efficiency was obtained froma 1.0 mmol scale reaction (entry 3). Both electron-withdrawinggroups (e.g., Br, aldehyde, ester, cyano, and amide, entries 1, 2,and 4–8) and electron-donating groups (e.g., methyl, methoxy,and ethoxy, entries 9 and 10) of the substrate were tolerant tothe electrocatalytic reaction. However, the yields and faradicefficiencies for electron-donating aryl alcohols (entries 9 and10) were slightly lower than those of electron-withdrawing arylalcohols (entries 1, 2, and 4–8). It may be because theelectron-donating aryl alcohols were further oxidized on the

1

2

6

anode due to their lower oxidation potential. For the  $\pi$ conjugated aryl alcohols, the isolated yields and faradic efficiencies were also satisfactory (89% and 82% yield, 62% and 60% faradic efficiency for entries 11 and 12, respectively). Pinacol boronates were also active substrates for the electrocatalytic arylboronic acid hydroxylation. As shown in entry 13, 62% isolated yield and 54% faradic efficiency was obtained by using phenylboronic acid pinacol ester as the starting material.

With the advantages of the facile setup and high yield, the electrocatalytic arylboronic acid hydroxylation can be applied to large-scale reactions. For example, a 5.0 g (41.0 mmol) scale reaction of PhB(OH)<sub>2</sub> (Table 1, entry 3) was conducted under the same conditions with a slightly lower isolated yield than that of the 1.0 mmol scale reaction (66% yield and 62% faradic efficiency), likely because of the oxidation of phenol during a longer reaction time. When the potentiostatic electrolysis was applied to a 50 g (0.33 mol) scale reaction of 4-formylphenylboronic acid, a higher yield and faradic efficiency than those of the 1.0 mmol scale reaction were obtained (90% yield and 71% faradic efficiency).

To gain in-depth understanding of the electrochemical reaction process, a systematic kinetic study was conducted. When the CV curves were recorded in an  $O_2$  saturated DMF solution with 2.5 mM MV(PF<sub>6</sub>)<sub>2</sub>, the catalytic current kept increasing with increasing PhB(OH)<sub>2</sub> (Figure S5a). The same tests were carried out in a DMF solution of 2.5 mM MV(PF<sub>6</sub>)<sub>2</sub> and 0.1 M PhB(OH)<sub>2</sub> with increasing  $O_2$  partial pressure (Figure S5c) and in a 0.1 M PhB(OH)<sub>2</sub> solution with the addition of MV(PF<sub>6</sub>)<sub>2</sub> under  $O_2$  (Figure S5e) or air (Figure S6). In each case, the catalytic current increased as the concentration of PhB(OH)<sub>2</sub>,  $O_2$ , or MV(PF<sub>6</sub>)<sub>2</sub> was increased.

$$i_{\rm cat}/i_{\rm p} = (n/0.4463)(RTk_{\rm obs}/F\nu)^{1/2}$$
 (1)

The turnover frequency (TOF, i.e.,  $k_{obs}$ ) of the electrocatalytic reaction under pseudo-first-order conditions can be calculated using the ratio of  $i_{cat}/i_p$  using eq (S1).<sup>14</sup> Here,  $i_{cat}$  is the catalytic current and  $i_p$  is the peak current for the reduction of  $MV^{2+}$ ,  $k_{obs}$  is the first order rate constant, F is Faraday constant,  $\nu$  is the CV scan rate, R is the gas constant, and n equals 1 for one electron process. The  $MV^{2+}/O_2/PhB(OH)_2$ system with 2.5 mM  $MV^{2+}$  and 0.1 M PhB(OH)<sub>2</sub> exhibited TOF of 16.1 s<sup>-1</sup> under O<sub>2</sub> (4.8 s<sup>-1</sup> under air); however, in the absence of MV<sup>2+</sup> catalyst, the reductive current just slightly increased (Figure 1a and 1b). With a PhB(OH)<sub>2</sub> concentration from 0 to 100 mM, a plot of the TOF versus  $PhB(OH)_2$ concentration is linear (Figure S5b), indicating that the catalytic rate is first order in  $PhB(OH)_2$ , giving a rate constant as  $k = 1.8 \times 10^2 \text{ s}^{-1} \cdot \text{M}^{-1}$ . Similarly, the first order of the catalytic rate in O2 was indicated by the linear relation of TOF versus O<sub>2</sub> partial pressure (Figure S5d). The first order of the catalytic rate in both  $PhB(OH)_2$  and  $O_2$  implied that the arylboronic acids hydroxylation reaction was not carried out through a stepwise oxygen-reduction/arylboronic acid-hydroxylation mechanism as proposed previously.<sup>13a,b</sup> Instead, a  $MV^{2+}/O_2/PhB(OH)_2$  three-component reaction was a key elementary reaction. In a control experiment, the obvious <sup>1</sup>H NMR spectroscopic changes of  $PhB(OH)_2$  in  $CD_3CN$  were observed by bubbling with  $O_2$  (Figure S7). Specifically, a new set of phenyl proton resonances were observed at  $\delta = 7.79$ , 7.49, and 7.41 ppm in comparison to the original set of phenyl proton resonances signal at  $\delta$  = 8.28, 7.68, and 7.59 ppm. We propose that there is a Lewis acid/base adduct formed between

 $PhB(OH)_2$  (Lewis acid) and  $O_2$  (Lewis base) (see Scheme 1). The Lewis basic  $O_2$  is believed to add to the vacant p-orbital of

Scheme 1. Proposed Mechanism for the Electrocatalytic Arylboronic Acid Hydroxylation



the Lewis acidic boron. Under both air and  $O_2$  atmosphere, the catalytic current also exhibited a linear relationship with the concentration  $MV(PF_6)_2$  (Figure S5f), indicating a single catalyst based mechanism.

According to the information obtained from the above electrochemical studies and control experiments, the reaction mechanism of the electrocatalytic arylboronic acids hydroxylation is proposed in Scheme 1. PhB(OH)<sub>2</sub> first formed an adduct with  $O_2$ , and then the  $PhB(OH)_2-O_2$  adduct was reduced by MV<sup>•+</sup>, which comes from the electrochemical reduction of  $MV^{2+}$  at -0.92 V (vs  $Cp_2Fe^{+/0}$ ). This homogeneous electron-transfer reaction would recover MV<sup>2+</sup> and generate a  $PhB(OH)_2$ - $O_2^{\bullet-}$  radical anion. The subsequent abstraction of a hydrogen atom and then 1,2-aryl shift proceeded to give the final phenolic product. Et<sub>3</sub>N was oxidized in the anodic process followed by a hydrogen atom transfer step to generate an iminium cation. Our proposed mechanism was further supported by the in situ <sup>1</sup>H NMR study (Figure S1). In the previous proposed photocatalytic mechanism,<sup>13a,b</sup> the reduction of  $O_2$  to  $O_2^{\bullet-}$  takes place first, and then the resulting  $O_2^{\bullet-}$  will react with PhB(OH)<sub>2</sub> to form  $PhB(OH)_2 - O_2^{\bullet-}$  radical anion. Thanks to the advantages of molecular electrocatalysis, the new mechanism based on the formation and reduction of the  $PhB(OH)_2 - O_2$  adduct was discovered and elucidated the catalytic nature of aerobic hydroxylation of arylboronic acids.

In summary, we report an electrochemical approach for aerobic hydroxylation of arylboronic acids to aryl alcohols catalyzed by methyl viologen  $(MV^{2+})$  that acts as an electrontransfer mediator to reduce an arylboronic acid-O<sub>2</sub> adduct to an arylboronic  $acid-O_2^{\bullet-}$  radical anion, a key elementary reaction. The reduction potential of  $O_2$  was reduced by 0.4 V in the presence of  $MV^{2+}$  and an arylboronic acid while the faster rate of the reduction of O2 was achieved through MV2+ catalysis. The wide substrate scope, satisfactory yield and faradic efficiency, and facile experimental setup as well as the low cost catalyst makes the electrocatalysis a promising approach for arylboronic acids hydroxylation. In light of the high activity and broad applications of  $O_2^{\bullet-}$  in organic synthesis, the simple and benign  $MV^{2+}/O_2$  electrocatalytic system has great potential to be applied in other organic transformations that are currently underway in our laboratory.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.7b02483.

Experimental details and additional figures (PDF)

# AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: leoliu@usu.edu.

### ORCID <sup>®</sup>

T. Leo Liu: 0000-0002-3698-1096

#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) (a) Morales-Guio, C. G.; Stern, L.-A.; Hu, X. Chem. Soc. Rev. 2014, 43, 6555. (b) Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W. Chem. Rev. 2015, 115, 12974. (c) Costentin, C.; Robert, M.; Saveant, J. M. Chem. Soc. Rev. 2013, 42, 2423.

(2) (a) Moeller, K. D. *Tetrahedron* 2000, 56, 9527. (b) Sperry, J. B.; Wright, D. L. *Chem. Soc. Rev.* 2006, 35, 605. (c) Yoshida, J.; Kataoka, K.; Horcajada, R.; Nagaki, A. *Chem. Rev.* 2008, 108, 2265.

(3) (a) Francke, R.; Little, R. D. Chem. Soc. Rev. 2014, 43, 2492. (b) Horn, E. J.; Rosen, B. R.; Baran, P. S. ACS Cent. Sci. 2016, 2, 302.

(c) Waldvogel, S. R.; Janza, B. Angew. Chem., Int. Ed. 2014, 53, 7122.
(4) (a) Frontana-Uribe, B. A.; Little, R. D.; Ibanez, J. G.; Palma, A.; Vasquez-Medrano, R. Green Chem. 2010, 12, 2099. (b) Rosen, B. R.; Werner, E. W.; O'Brien, A. G.; Baran, P. S. J. Am. Chem. Soc. 2014, 136, 5571. (c) Horn, E. J.; Rosen, B. R.; Chen, Y.; Tang, J.; Chen, K.; Eastgate, M. D.; Baran, P. S. Nature 2016, 533, 77. (d) Badalyan, A.; Stahl, S. S. Nature 2016, 535, 406.

(5) Schafer, H. J.; Harenbrock, M.; Klocke, E.; Plate, M.; Weiper-Idelmann, A. Pure Appl. Chem. 2007, 79, 2047.

(6) (a) Wang, P.; Tang, S.; Huang, P.; Lei, A. Angew. Chem., Int. Ed. 2017, 56, 3009. (b) Waldvogel, S. R.; Selt, M. Angew. Chem., Int. Ed. 2016, 55, 12578. (c) Zhou, H.; Shen, Y.; Xi, J.; Qiu, X.; Chen, L. ACS Appl. Mater. Interfaces 2016, 8, 15369.

(7) (a) Hickey, D. P.; Schiedler, D. A.; Matanovic, I.; Doan, P. V.; Atanassov, P.; Minteer, S. D.; Sigman, M. S. J. Am. Chem. Soc. 2015, 137, 16179. (b) Fuchigami, T.; Mitomo, K.; Ishii, H.; Konno, A. J. Electroanal. Chem. 2001, 507, 30. (c) Wei, Q.; Chen, J. R.; Hu, X. Q.; Yang, X. C.; Lu, B.; Xiao, W. J. Org. Lett. 2015, 17, 4464. (d) Zhu, L.; Xiong, P.; Mao, Z. Y.; Wang, Y. H.; Yan, X.; Lu, X.; Xu, H. C. Angew. Chem., Int. Ed. 2016, 55, 2226.

(8) (a) Hu, B.; DeBruler, C.; Rhodes, Z.; Liu, T. L. J. Am. Chem. Soc. 2017, 139, 1207. (b) Hu, B.; Seefeldt, C.; DeBruler, C.; Liu, T. J. Mater. Chem. A 2017, 5, 22137. (c) Liu, T.; Wei, X.; Nie, Z.; Sprenkle, V.; Wang, W. Adv. Energy Mater. 2016, 6, 1501449.

(9) (a) Park, J. W.; Choi, M. H.; Park, K. K. Tetrahedron Lett. 1995, 36, 2637. (b) Dicosimo, R.; Wong, C. H.; Daniels, L.; Whitesides, G. M. J. Org. Chem. 1981, 46, 4622. (c) Maeda, H.; Kajiwara, S. Biotechnol. Bioeng. 1985, 27, 596.

(10) Bird, C. L.; Kuhn, A. T. Chem. Soc. Rev. 1981, 10, 49.

(11) Hayyan, M.; Hashim, M. A.; AlNashef, I. M. Chem. Rev. 2016, 116, 3029.

(12) (a) Su, C. L.; Acik, M.; Takai, K.; Lu, J.; Hao, S. J.; Zheng, Y.; Wu, P. P.; Bao, Q. L.; Enoki, T.; Chabal, Y. J.; Loh, K. P. *Nat. Commun.* **2012**, *3*, 1298. (b) Johnson, J. A.; Luo, J.; Zhang, X.; Chen, Y. S.; Morton, M. D.; Echeverria, E.; Torres, F. E.; Zhang, J. ACS *Catal.* **2015**, *5*, 5283. (c) Miyata, A.; Murakami, M.; Irie, R.; Katsuki, T. Tetrahedron Lett. **2001**, *42*, 7067.

(13) (a) Luo, J.; Zhang, X.; Zhang, J. ACS Catal. 2015, 5, 2250.
(b) Zou, Y. Q.; Chen, J. R.; Liu, X. P.; Lu, L. Q.; Davis, R. L.; Jorgensen, K. A.; Xiao, W. J. Angew. Chem., Int. Ed. 2012, 51, 784.
(c) Inamoto, K.; Nozawa, K.; Yonemoto, M.; Kondo, Y. Chem. Commun. 2011, 47, 11775. (d) Xu, J. M.; Wang, X. Y.; Shao, C. W.; Su, D. Y.; Cheng, G. L.; Hu, Y. F. Org. Lett. 2010, 12, 1964. (e) Prakash, G. K. S.; Chacko, S.; Panja, C.; Thomas, T. E.; Gurung, L.; Rasul, G.; Mathew, T.; Olah, G. A. Adv. Synth. Catal. 2009, 351, 1567.
(f) Kianmehr, E.; Yahyaee, M.; Tabatabai, K. Tetrahedron Lett. 2007, 48, 2713. (g) Simon, J.; Salzbrunn, S.; Prakash, G. K. S.; Petasis, N. A.; Olah, G. A. J. Org. Chem. 2001, 66, 633. (h) Maleczka, R. E., Jr.; Shi, F.; Holmes, D.; Smith, M. R., 3rd J. Am. Chem. Soc. 2003, 125, 7792.
(14) (a) Saveant, J. M. Chem. Rev. 2008, 108, 2348. (b) Martin, D. J.; McCarthy, B. D.; Rountree, E. S.; Dempsey, J. L. Dalton Trans. 2016, 45, 9970.