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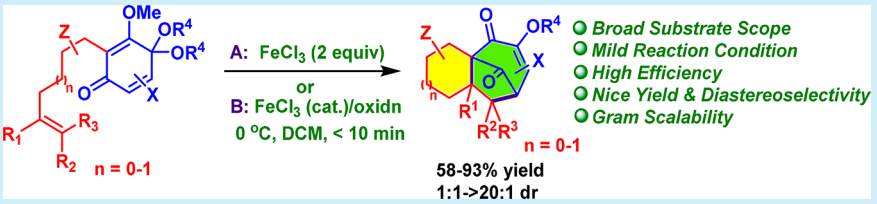
Iron-Catalyzed Intramolecular Perezone-Type [5 + 2] Cycloaddition: Access to Tricyclo[6.3.1.0^{1,6}]dodecane

Yongjiang Liu,[†] Xiao Wang,[†] Song Chen,[†] Shaomin Fu,[†] and Bo Liu*[,†,‡]

[†]Key Laboratory of Green Chemistry &Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China

[‡]State key Laboratory of Natural Medicines, China Pharmaceutical University, Nanjing 210009, China

Supporting Information



ABSTRACT: An iron-catalyzed perezone-type [5 + 2] cycloaddition toward tricyclo[6.3.1.0^{1,6}]dodecane scaffolds is presented, furnishing cycloadducts with two new C−C bonds and three to four stereogenic centers generated with typically good yields and excellent diastereoselectivities. Two independent conditions, catalytic $FeCl_3$/$PhCO_3tBu$ (0.5 equiv/1 equiv) and stoichiometric $FeCl_3$(2 equiv), have been respectively manifested to be applicable for various substrates. Mechanistically, the reaction may proceed via iron-mediated generation of a carbon cationic center, which triggers subsequent [5 + 2] cyclization. Derivation of the cycloadduct was conducted to testify the applicability of this method.

Pharmaceutical ingredients and natural products embodying diverse tricyclo[6.3.1.0^{1,6}]dodecane subunits have been floating throughout the literature with a remarkable range of biological activities. As highlighted in Figure 1, campylopin (**1**)

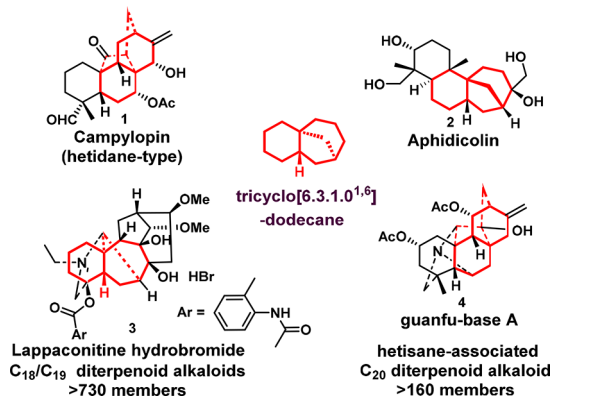


Figure 1. Structures of tricyclo[6.3.1.0^{1,6}]dodecane and related natural products.

and its analogues, for example, function as the selective antagonists of the neuronal α7 nAChR receptors, which hold promise as an agent in the treatment of Alzheimer's disease.[1] Aphidicolin (**2**), a DNA polymerase inhibitor, shows antiviral activity against human herpes viruses.[2a,b] Lappaconitine hydrobromide (**3**), a C_{18}-diterpenoid alkaloid, possesses remarkable anti-inflammatory activity and is eight times more potent than cocaine as an anesthetic in the rabbit cornea model.[2c,d] Guaufu base A (**4**), isolated from *Aconitum coreanum*, was reported to exhibit antiarrhythmic activities.[2e]

Synthetically, the above core tricyclo[6.3.1.0^{1,6}]dodecane motif could be accessible via intramolecular perezone-type [5 + 2] cycloaddition.[3] Although the identical strategy has been extensively implemented to forge tricyclo[5.3.1.0^{1,5}]undecane subunits and related natural product syntheses, further expansion to the tricyclo[6.3.1.0^{1,6}]dodecane skeleton was not successful (Scheme 1a). To date, only two cases of intramolecular perezone-type [5 + 2] cycloaddition toward tricyclo[6.3.1.0^{1,6}] dodecane have been documented, including $LiClO_4$/TMSOTf-promoted cyclization from the Grieco group[4] and anionic oxidation enabled ring formation by the Yamamura group.[5] Both studies resulted in either moderate yields or very limited substrate scope (Scheme 1b). This insufficiency can be ascribed to the relatively slower cyclization rate to form a six-membered ring than that in robust formation of a five-membered ring, which hinted at a synthetic challenge and deserved further insightful investigation. Recently, our group became captivated by tricyclo[6.3.1.0^{1,6}]dodecane subunits on account of their exquisite structure and potent biological activities. We now present our discovery on an iron-catalyzed intramolecular perezone-type [5 + 2] cycloaddition toward tricyclo[6.3.1.0^{1,6}]dodecane compounds with satisfactory yields, diastereoselectivities, and broad substrate scope (Scheme 1c).

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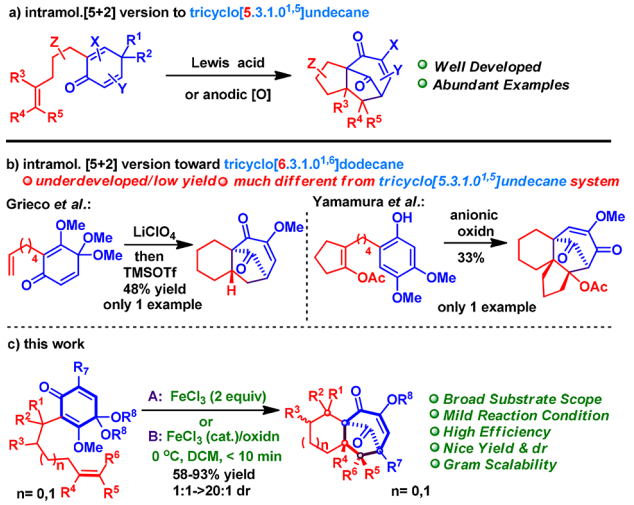
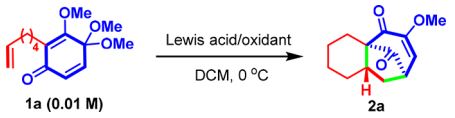
Scheme 1. Progress in Synthetic Reactions Involving Perezone-Type [5 + 2] Cycloaddition



Because the corresponding intramolecular cycloaddition toward tricyclo[5.3.1.0^{1,5}]undecane has been well developed,[3a] we focused our attention on intramolecular perezone-type [5 + 2] cycloaddition toward tricyclo[6.3.1.0^{1,6}]dodecane. Initially, we screened a number of Lewis acid catalysts, but they gave poor results (Table 1, entries 1−5; see the Supporting Information (SI) for more details). We then discovered that iron has been extensively applied as an abundant and environmentally benign catalyst or promoter in organic synthesis,[6] especially in several cycloaddition reactions.[7] $FeCl_3$ (2 equiv) was then tested and found to promote the desired cycloaddition product **2a** at −78 °C, albeit in 20% yield (Table 1, entry 6). Although $SnCl_4$ also gave a comparable yield (20%) under identical conditions, $FeCl_3$ could give a higher product yield than $SnCl_4$ at elevated temperature (Table 1, entries 7−9). In addition, higher catalyst loading did not increase the yield, and lower loading reduced the yield (see the SI for details). Furthermore, $FeCl_3{\cdot}6H_2O$ delivered cycloadducts in 35% yield (Table 1, entry 10), indicating the need for anhydrous $FeCl_3$. Iron(III) triflate, a stronger Lewis acid than $FeCl_3$, proved inefficient, generating a complex mixture. Other iron(III) and iron(II) Lewis acids could not catalyze this cycloaddition reaction under the conditions we tested (Table 1, entries 11−13; see the SI for details).

Next, we screened various additives to determine whether or not they might assist $FeCl_3$ and thus reduce the amount of iron(III) catalyst needed. Interestingly, we discovered that oxidizing additives strongly influenced the cycloaddition with use of 0.2 equiv of $FeCl_3$ as the catalyst. Of the various oxidants (2.5 equiv) tested, only DDQ, CAN, and $PhCO_3tBu$ afforded the desired cycloadducts in respective yields of 62%, 22%, and 66% (Table 1, entries 14−18; see the SI for details). Prudent augmentation of $FeCl_3$ to 50 mol % could enable higher reactivity (79% yield, Table 1, entry 19). The optimal yield of 81% was achieved by using 0.5 equiv of $FeCl_3$ and 1 equiv of $PhCO_3tBu$ (Table 1, entry 20).[8] Delightfully, the reaction performed on a 2.3 g scale proceeded smoothly (Table 1, entry 21). Using either $FeCl_3$ or $PhCO_3tBu$ on its own did not support the reaction (Table 1, entries 22 and 23). Notably, our extensive study on the transformation of 1,4-benzoquinones **2′** to **2a′** with various catalysts was unsuccessful,[9] although several studies achieved intermolecular cycloaddition reactions using

Table 1. Screening of Reaction Conditions



entry[a]	Lewis acid (*x* equiv)	temp (°C)	oxidant[b] (2.5 equiv)	yield[c] (%)
1	$InBr_3$(2.0)	−40		CM
2	BBr_3 (2.0)	−40		CM
3	$ZrCl_4$ (2.0)	−78 to rt		CM
4	Et_2AlCl (2.0)	−78 to rt		NR
5	$LaCl_3{\cdot}LiCl$ (2.0)	−78 to rt		NR
6	$FeCl_3$ (2.0)	−78		20
7	$SnCl_4$(2.0)	−78		20
8	$SnCl_4$ (2.0)	0		45
9[d]	**$FeCl_3$ (2.0)**	**0**		**83**
10	$FeCl_3{\cdot}6H_2O$ (2.0)	0		35
11	$Fe(OTf)_3$ (2.0)	0		CM
12	$Fe(acac)_3$ (2.0)	0		NR
13	$Fe(OTf)_2$ (2.0)	0		NR
14	$FeCl_3$ (0.2)	0	O_2 (balloon)	CM
15	$FeCl_3$ (0.2)	0	$(iPrO)_2$	CM
16	$FeCl_3$ (0.2)	0	CAN	22
17	$FeCl_3$ (0.2)	0	DDQ	62
18	$FeCl_3$ (0.2)	0	$PhCO_3tBu$	66
19	$FeCl_3$ (0.5)	0	$PhCO_3tBu$	79
20[e]	**$FeCl_3$ (0.5)**	**0**	**$PhCO_3tBu$ (1.0)**	**81**
21[f]	$FeCl_3$ (0.3)	0	$PhCO_3tBu$ (1.0)	63
22	$FeCl_3$ (0.5)	0		18
23		0	$PhCO_3tBu$	NR

[a]Reactions were performed on a 0.19 mmol scale. [b]2.5 equiv of oxidant was added unless otherwise stated. [c]Isolated yield after full conversion of **1a** (TLC control). NR, no reaction; CM, complex mixture. [d]Defined as conditions A. [e]Defined as conditions B. [f]Gram scale (2.3 g of **1a**).

unmasked *p*-benzoquinones and aromatic alkenes toward bicyclo[3.2.1]octane or using intramolecular cycloaddition reactions with unmasked *p*-benzoquinones as substrates toward tricyclo[5.3.1.0^{1,5}]undecane.[3a] Our results reveal the particularity of intramolecular perezone-type [5 + 2] cycloaddition toward tricyclo[6.3.1.0^{1,6}]dodecane.

From the reaction conditions shown in Table 1, we selected the conditions in entry 9 as conditions A and those in entry 20 as conditions B and then examined the substrate scope of the [5 + 2] cycloaddition under these two sets of conditions. Conditions A and B were compatible with a wide range of substrates with different chain lengths, various substitutions on the chain tether, and diverse alkenes (Scheme 2). Under both conditions A and B, the reaction could be extended to afford cycloadduct **2b** as well with the tricyclo[5.3.1.0^{1,5}]undecane motif, indicating general applicability. Even after the methoxyl ketal was changed to an allyloxyl ketal, both conditions proved effective at generating **2c** in comparable yield (79%, 72%) with excellent dr (>20:1). Furthermore, chain substitution adjacent to the benzoquinone ring proceeded with remarkable stereochemical control during cycloaddition, furnishing compounds **2d** and **2e** with decent diastereoselectivity. However, substitution distant from the benzoquinone ring did not proceed with satisfactory diastereoselectivity, such as in the reaction to generate **2f** (dr = 1:1). Notably, the substrates scope could be extensively broadened to diverse alkenes, including

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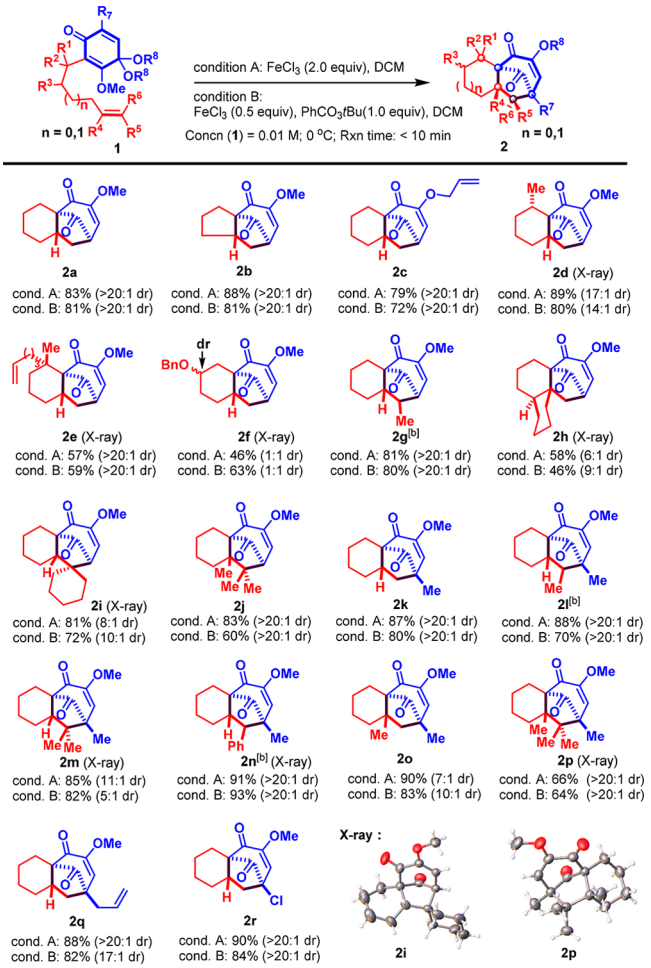
Scheme 2. [5 + 2] Cycloaddition toward Tricyclo[6.3.1.0^{1,6}][a]

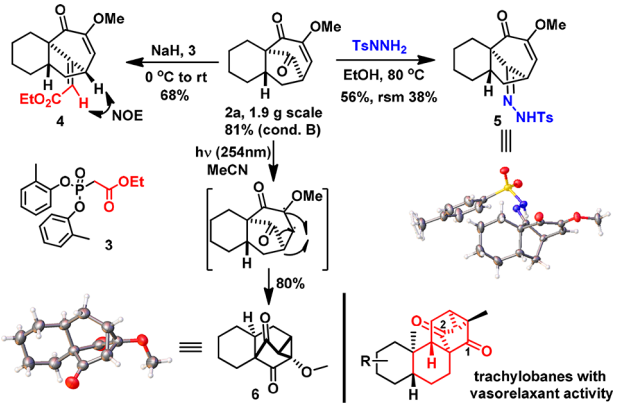


[a]Isolated yield. [b]The *E*-alkene of **1g,l,n** were submitted to this reaction.

trans-disubstituted, *gem*-disubstituted, and tri- and tetrasubstituted alkenes, leading to cycloadduct products featuring several contiguous tertiary or quaternary stereogenic centers (**2g−j,l−o**) with 46−93% yields and 6:1 to >20:1 diastereoselectivities. After that, we were curious about how various substituents on the benzoquinones would impact the efficiency of cycloaddition. Gratifyingly, adding a methyl group on the benzoquinone maintained the reactivity (**2k**, 80−87% yield, >20:1 dr). Furthermore, varying the methyl substituent on benzoquinone to allyl or chloride resulted in the corresponding cycloadducts **2q** and **2r** with comparable yields (82−90%) and decent diastereoselectivities (17:1 to >20:1).[10] Surprisingly, even compound **2p**, with four contiguous quaternary carbon centers, could be assembled as a single diastereomer. Unfortunately, a further survey on substrates with heteroatom on tethered alkyl chain does not furnish the desired [5 + 2] cycloproduct (see the SI for details).

The [5 + 2] cycloadducts constructed by our approach consist of several functional groups that could be exploited for further transformations (Scheme 3). In the presence of base, Horner−Wadsworth−Emmons reaction of compound **2a** with the phosphate **3** selectively transformed the ketone on the bridge into a *Z*-alkene, affording compound **4**, the structure of which was confirmed by NOE experiments. Moreover, selective

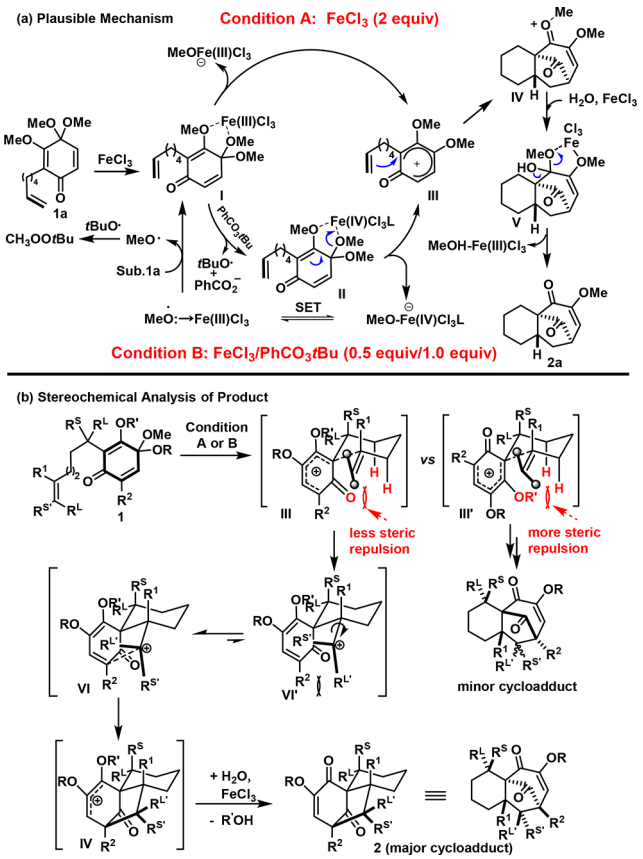
Scheme 3. Derivatization of Compounds Obtained Using Iron-Catalyzed Intramolecular Perezone-Type [5 + 2] Cycloaddition



hydrazone formation gave compound **5** whose structure was confirmed via NMR analysis and X-ray crystallography. In addition, photoirradiation of **2a** produced compound **6** after skeleton rearrangement of a diradical intermediate. The structure of **6**, confirmed by X-ray crystallography, was of potential value for accessing trachylobanes with vasorelaxant activity.[11]

A tentative mechanism for the present Fe-catalyzed [5 + 2] cycloaddition is depicted in Scheme 4a. The reaction commenced with complexation of substrate **1a** with $FeCl_3$ to configure a five-membered didentated intermediate **I**. Under

Scheme 4. Plausible Mechanism and Stereochemical Analysis of Product



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conditions A, excess $FeCl_3$ was capable of extracting OMe to form the anionic $[MeO\text{-}FeCl_3]^-$ and the cationic intermediate **III**. Alternatively, under conditions B, Fe(III) complex **I** might be initially oxidized to Fe(IV) species **II**.[12] The Fe(IV) species **II** held stronger Lewis acidity, which was beneficial to eliminate a CH_3O group on the masked benzoquinone, leading to the cationic **III** and the anionic $[CH_3O\text{-}Fe(IV)Cl_3L]^-$. The above alkoxyl Fe(IV) species was supposed to be unstable and would undergo SET to give rise to $CH_3{-}\dot{O}{:}\ {\rightarrow}Fe(III)Cl_3$.[13] This radical Fe(III) species would further act on substrate **1a** via ligand exchange to release the radical $CH_3O^{\bullet}$, which was subsequently captured by tBuO$^{\bullet}$ to result in CH_3OOtBu and regenerate intermediate **I**. Accordingly, reactions in both conditions might share the same pathway involving the intermediate **III**, which could lead to the following stepwise electrophilic [5 + 2] cycloaddition to give the intermediate **IV**. Final demethoxylation aided by H_2O and $FeCl_3$ could furnish the cycloadduct **2a**.[14]

Furthermore, we rationalized the stereochemistry of the cycloadducts (Scheme 4b). Exposure of compound **1** under conditions A or B results in the intermediate **III** or **III′**. The presence of [1, 3] axial repulsion in the chair conformation of the cyclohexane in the transition state favors the pathway involving the intermediate **III**, which harbors a less bulky R^S at the axial position. Otherwise, more steric repulsion in intermediate **III′** resulted in the minor cycloadduct. In the pathway involving intermediate **III**, the first intramolecular cyclization generates intermediate **VI′** through a cationic 6-*exo*-*trig* mode, in which steric repulsion between R^2 and R^L drives single bond rotation to furnish intermediate **VI**. A second intramolecular cyclization gives intermediate **IV**, which subsequently undergoes demethoxylation under $FeCl_3$ to furnish compound **2** as the major cycloadduct.

In conclusion, we have developed an iron-catalyzed intramolecular perezone-type [5 + 2] cycloaddition toward tricyclo[6.3.1.$0^{1,6}$]dodecane. The efficacy of our approach, coupled with the existence of various functional group handles for further transformation in the tricyclo[6.3.1.$0^{1,6}$]dodecane motif, will definitely enable its application in total synthesis of related pharmaceutically useful compounds and natural products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00989.

Detailed experimental procedures, spectroscopic data, ^1H and ^{13}C NMR spectra and X-ray crystallographic data of new compounds (PDF)

Accession Codes

CCDC 1524256−1524259, 1524261, 1524263−1524264, 1524266, 1524269, and 1529719 contain 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

*E-mail: chembliu@scu.edu.cn.

ORCID

Bo Liu: 0000-0002-6235-1573

Notes

The authors declare no competing financial interest.

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For a recent review article, see: (d) Wang, C.; Wan, B. *Chin. Sci. Bull.* **2012**, *57*, 2338.

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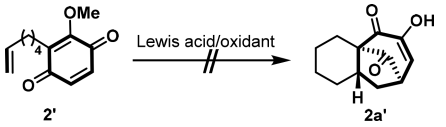
(8) ICP-OES analysis of our $FeCl_3$ catalyst reveals it contains Cu, Ni, Al, Ti, Cr, Zn, Mg, Ca, and Mn. However, the corresponding chloride salts of these metals displayed no activity or very weak activity to promote intramolecular [5 + 2] cycloaddition of **1a**. See the SI for details.

(9) We also exerted extensive study on the transformation of 1,4-benzoquinones **2′** to cycloadduct **2a′** with various Lewis acids, but failed. See the SI for details.



(10) Relative stereochemistry of the cycloadducts **2d**, **2e**, **2f**, **2h**, **2i**, **2m**, **2n**, and **2p** was determined by X-ray crystallography. The relative configuration of other cycloadducts was confirmed by analogy accordingly.

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(13) A similar TEMPO-Fe(III)Cl_3 complex was reported by Hayton et al.; see: Scepaniak, J. J.; Wright, A. M.; Lewis, R. A.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2012**, *134*, 19350.

(14) For the related control experiments, see the SI for details.

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