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Active Cp*Iridium(III) Complex with *ortho*-Hydroxyl Group Functionalized Bipyridine Ligand Containing an Electron-Donating Group for the Production of Diketone from 5-HMF

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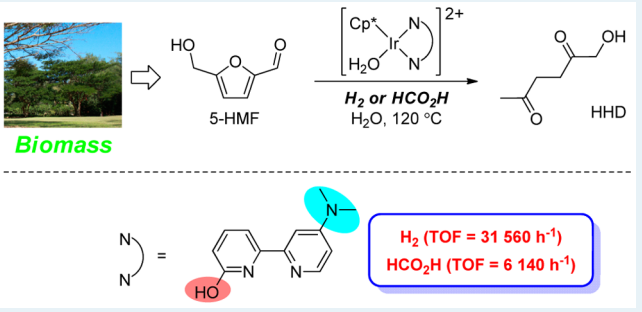
Supporting Information

ABSTRACT: Diketones are ubiquitous blocks for organic synthesis. This work shows a highly active catalyst for the production of diketone 1-hydroxyhexane-2,5-dione (HHD) by hydrogenation of 5-hydroxymethylfurfural (5-HMF), a bio-based platform chemical. Half-sandwich Cp*Ir complexes with *ortho*-hydroxyl group functionalized bipyridine ligands were synthesized and found to exhibit remarkably high catalytic activity for this reaction in acidic water. The HHD formation rate was further increased when the bipyridine ligands of Cp*Ir complexes were modified by an electron-donating group. A bipyridine ligand with both dimethylamino and *ortho*-hydroxyl groups achieved a HHD formation turnover frequency (TOF) of 31 560 h^{-1} by H_2 and a TOF of 6140 h^{-1} by formic acid, representing 180-fold and 3 000-fold over the activities of the best reported results, respectively.



KEYWORDS: *biomass, hydrogenation, iridium, 5-HMF, ketone*

The abundant cellulosic biomass provides a renewable alternative feedstock to the declining fossil carbon sources for the production of chemicals and fuels. A sustainable process to produce valuable chemicals depends on the development of new enabling technologies for efficient conversions of biobased feedstock. 5-Hydroxymethylfurfural (5-HMF) has been known as a potential platform chemical for the synthesis of a wide range of chemicals.[1−6] 1-Hydroxyhexane-2,5-dione (HHD), one of the diketone derivatives, was recently synthesized from 5-HMF.[7] HHD could also serve as a potential feedstock for the production of a number of fine chemicals. Some examples are shown in Scheme 1. HHD can be hydrogenated to 1,2,5-hexanetriol,[8] a precursor to spiroketals. HHD was recognized as the in situ-generated intermediate from 5-HMF for the formation of cyclopentanone-based chemicals through Aldol condensation.[9,10] Oxidation of HHD may produce levulinic acid.[11] HHD may also be a potential candidate of hexane-2,5-dione,[12,13] a reactant for Paal-Knorr pyrrole synthesis.

Recently, catalytic production of HHD from 5-HMF has been studied by several groups. Heterogeneous catalysts[10,14,15] including Pd/C and Au/Nb_2O_5 were shown to catalyze HHD production with the assistance of acid under H_2. Ru complexes[16,17] also catalyzed HHD formation from 5-HMF by hydrogenation with formic acid. However, these reaction systems showed low catalyst activity, with the calculated turnover frequency (TOF) based on the reported results was less than 40 h^{-1} (Table 1, entries 1−4). We recently found that bipyridine coordinated Cp*Ir complex efficiently catalyzed the hydrogenation/hydrolysis of 5-HMF in water under H_2.[7] In that work, 5-HMF underwent acid-catalyzed hydrolysis, followed by Cp*Ir-catalyzed hydrogenation to generate HHD. The Cp*Ir complex is much more active (Table 1, entry 5, TOF reached to 173 h^{-1}) than the heterogeneous catalysts and works even under low H_2 pressure. To further improve the economics of HHD production, in this work, we designed and synthesized half-sandwich Cp*Ir complexes with functional ligands for 5-HMF hydrogenation in acidic water.

ortho-Hydroxyl (*o*-OH) group functionalized bipyridine reversibly generates hydroxyl, keto, and oxyanion structure (Scheme 2). Cp*Ir complexes coordinated by the *o*-OH functionalized bipyridine ligands show unique catalytic properties, including dehydrogenation of alcohol and nitrogen heterocycles,[18−25] CO_2 hydrogenation and formic acid decomposition,[26−34] water oxidation,[35,36] α-alkylation of ketones,[37,38] and aldehyde−water shift reaction.[39,40] In general, bipyridine bearing an *o*-OH group significantly improves the hydrogenation ability of Cp*Ir complex: (1) Under basic conditions, the strong electron-donating oxyanion group improves the CO_2 hydrogenation activity; (2) *ortho*-Oxyanion serves as a pendent base to assist H_2 heterolytic dissociation under basic conditions; (3) Oxyanion is a water-soluble moiety.

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Scheme 1. Production of Chemicals from 5-HMF via HHD

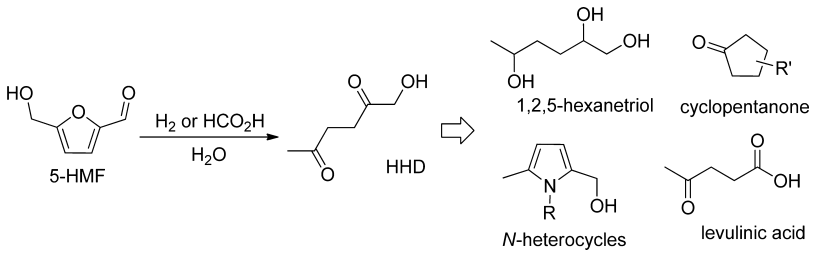
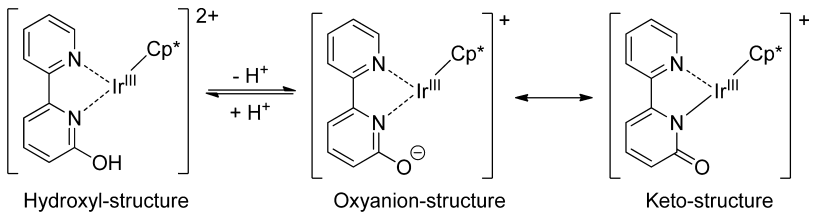


Table 1. Hydrogenation of 5-HMF to HHD through Heterogeneous and Homogeneous Catalysis

entry	catalyst	conditions	conversion (%)	selectivity (%)	TOF (h^{-1})	ref
1	Ru-complex	HCO_2H (12 equiv)/ 100 °C	>99	54	2	16
2	Pd/C	H_2 (50 bar)/ Amberlyst-15 (20 wt %)/ 80 °C	100	77	16	15
3	Pd/C	H_2 (10 bar)/ CO_2 (30 bar)/ 120 °C	100	77	12	14
4	Au/Nb_2O_5	H_2 (80 bar)/ H_3PO_4 (8.5 mM)/ 140 °C	81	74	35	10
5[a,b]	Cp*Ir-bipyridine	H_2 (7 bar)/ 120 °C	>99	82.1	173	7
6[a,b]	Cp*Ir-L1	H_2 (10 bar)/ 120 °C	>99	81.0	162	this work
7[c,d]	Cp*Ir-bipyridine	H_2 (10 bar)/ 120 °C	10.2	<1	–	this work
8[c,d]	Cp*Ir-L1	H_2 (10 bar)/ 120 °C	55.8	45.7	5100	this work
9[c,d]	Cp*Ir-L2	H_2 (10 bar)/ 120 °C	33.1	52.0	3440	this work
10[c,d]	Cp*Ir-L3	H_2 (10 bar)/ 120 °C	60.1	46.8	5620	this work
11[c,d]	Cp*Ir-L4	H_2 (10 bar)/ 120 °C	42.7	71.4	6100	this work

[a]Catalyst (0.25 mol % to 5-HMF), and water (4.0 mL), at 120 °C for 2 h. [b]TOF is the average value of 1 h. [c]5-HMF (1.0 mmol), catalyst Cp*Ir-L (0.0025 mol % to 5-HMF), and aqueous solution (4.0 mL, pH = 3.0), under 10 bar of H_2, at 120 °C for 2 h. GC-MS yield, *N*,*N*-dimethylformamide is the internal standard. [d]TOF is the average value of 2 h.

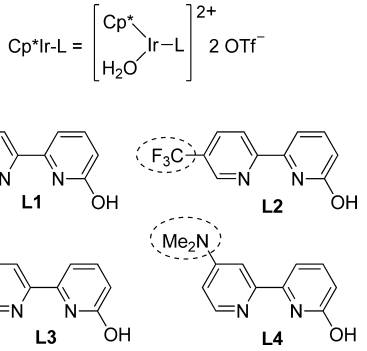
Scheme 2. Equilibrium of Bipyridine Ligand Bearing an *ortho*-Hydroxyl Group



To enhance the catalytic hydrogenation activity of Cp*Ir complex, considerable recent optimizations of bipyridine ligand[26,31] have been mainly focused on introducing more OH-groups and other nitrogen heterocycles such as pyrazole and pyrimidine.

Acidic conditions facilitate the synthesis of HHD from 5-HMF. According to the Hammett substituent constant,[41] oxyanion is a strong electron-donating group. However, in acidic water, the hydroxyl structure is dominant if the pH is lower than the pK_a of metal complex (Scheme 2). Dimethyl amino (NMe_2) group is much more electron-donating than hydroxyl group. As the *o*-OH group may promote the Cp*Ir complex-catalyzed H_2 heterolytic dissociation, and because NMe_2 may strongly enhance the hydrogenation activity of Cp*Ir complex, in our ligand design strategy, we combined these two features into the bipyridine ligand and synthesized a new catalyst Cp*Ir-L4 (Scheme 3). Moreover, the effect of bipyridine ligand bearing electron-donating or -withdrawing group on the catalytic activity of Cp*Ir complex was less investigated. We also prepared two functionalized bipyridines

Scheme 3. Cp*Ir-L Complexes in This Study; Cp*Ir-L2, L3 and L4 Are New Structures



(L2 and L3) to systematically verify the electronic effect of ligand on the hydrogenation activity of the Cp*Ir complexes. The pK_a values of the above synthesized Cp*Ir complexes were measured through UV−vis absorption and Boltzmann function fitting (details are shown in Figures S1−S4, Supporting

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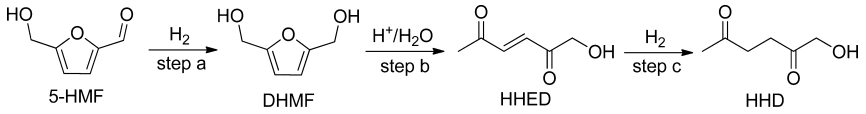
Scheme 4. Reaction Mechanism



Information). The pK_a value of Cp*Ir complex increases with more electron-donating group substituted ligand: p$K_a^{Cp*Ir-L2}$ (3.15) < p$K_a^{Cp*Ir-L1}$ (3.53) < p$K_a^{Cp*Ir-L3}$ (3.72) < p$K_a^{Cp*Ir-L4}$ (4.05). To explore the electronic effect of ligand on Ir metal, the chemical state of Cp*Ir complex was measured by XPS (details are shown in Figure S5, Supporting Information). The bonding energy of Ir $4f_{7/2}$ core level of Cp*Ir complex decreases with more electron-donating group substituted ligand: Cp*Ir-L2 (62.68 eV) > Cp*Ir-L1 (62.59 eV) > Cp*Ir-L3 (62.49 eV) > Cp*Ir-L4 (62.41 eV).

Among the reported results (Table 1, entries 1−5), Cp*Ir-bipyridine catalyst showed the best hydrogenation activity (entry 5). Cp*Ir-L1 also showed similar catalytic activity (entry 6). As 5-HMF is converted to HHD through hydrogenation and acid-catalyzed hydrolysis (Scheme 4), we optimized the conditions under acidic water (pH = 3). To compare the activities of Cp*Ir-bipyridine and Cp*Ir-L1, a low concentration of catalyst (0.0025 mol % to 5-HMF) was evaluated (entries 7 and 8) so that the intrinsic activities of the catalysts can be measured at a partial 5-HMF conversion level. A HHD yield of 25.5% was reached with Cp*Ir-L1 (entry 8), while the HHD concentration became below the GC-MS detection limit due to the low Cp*Ir-bipyridine loading (entry 7). It was noted that Cp*Ir-L1 exhibited a very high catalytic activity with a TOF of 5100 h^{-1} for HHD formation. The remarkably improved activity in entry 8 over that in entry 7 provides clear evidence in the effective heterolytic dissociation of H_2 due to the *o*-OH group in the functionalized ligand L1. The results are consistent with previous studied on the role of *o*-OH in facilitating heterolytic dissociation of H_2 for catalyzing the hydrogenation reaction as discussed above. The decreased HHD selectivity (entry 8 vs entry 6) was due to the formation of undetected humins, an acid-catalyzed Aldol condensation product.[42−44] The HHD selectivity was expected to improve by optimizing Cp*Ir catalyst and the pH. We then studied the electronic effect of ligand by adding electron-withdrawing and -donating groups to bipyridine. Ligands L2, L3, and L4 were synthesized by introducing trifluoromethyl (CF_3), methyl (Me), and NMe_2, respectively (entries 9−11). Compared to the TOF of 5100 h^{-1} with Cp*Ir-L1, the catalysts Cp*Ir-L3 and Cp*Ir-L4 with electron-donating groups Me and NMe_2 accelerated the reaction (entries 10 and 11), resulting in TOF of 5620 and 6100 h^{-1}, respectively. In contrast, the electron-withdrawing group CF_3 reduced the catalyst activity (3440 h^{-1}, entry 9). Moreover, Cp*Ir-L4 achieved an acceptable HHD selectivity of 71.4% (entry 11) even at the highest activity. It is therefore evident that the reaction rate is increased by increasing the electron density of the ligand (CF_3 < H < Me < NMe_2). As the XPS analysis of Ir showed that the electron-donating group increases the electron density at Ir, which consequently causes as increase in the electron density on Ir-hydride bond, favoring enhanced hydrogenation rate.

We then optimized pH to improve the catalytic performance of Cp*Ir-L4. As shown in Figure 1, with increasing the acidity from pH 7 to 2, the HHD selectivity first increases and then decreases. The best HHD yield (31.2%) with a high selectivity

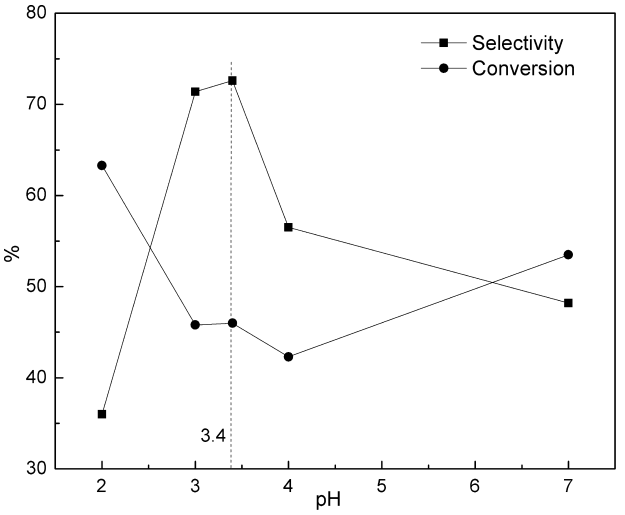


Figure 1. Optimization of pH for the catalytic performance of Cp*Ir-L4. Reaction conditions: 5-HMF (1.0 mmol), catalyst Cp*Ir-L4 (0.0025 mol % to 5-HMF), and aqueous solution (4.0 mL), under 10 bar of H_2, at 120 °C for 2 h. GC-MS yield, *N*,*N*-dimethylformamide was the internal standard.

(74.6%) was obtained at the pH near 3.4. A brief mechanism[7] of Cp*Ir complex catalyzed hydrogenation/hydrolytic ring opening of 5-HMF is shown in Scheme 4. Hydrogenation of 5-HMF (step a) produced 2,5-dihydroxymethylfuran (DHMF). DHMF underwent acid-catalyzed hydrolysis (step b) to form 1-hydroxyhex-3-ene-2,5-dione (HHED). Hydrogenation of HHED (step c) generated product HHD. In general, hydrolysis reaction (step b) may be slowed down with decreasing the solution acidity. However, hydrogenation reaction (steps a and c) may speed up with decreasing solution acidity, as strong acid may suppress the deprotonation of hydroxyl group to oxyanion group (Scheme 2). Thus, under strong acidic condition (pH is 2), the low HHD selectivity is mainly due to the slow hydrogenation reaction rate and the fast humins formation from Aldol-condensation of the feed and some intermediates such as HHED. On the other hand, at low acidity (pH is 7), 20.3% of DHMF was obtained, and thus, the low HHD selectivity is mainly because of the slow hydrolysis reaction.

We further optimized the H_2 pressure over the aqueous solution in the presence of Cp*Ir-L4 (Figure 2). The HHD formation rate reflected by the TOF increased significantly from 8720 h^{-1} to 26 880 h^{-1} with increasing H_2 pressure from 10 to 50 bar in the presence of 0.0025 mol % of Cp*Ir-L4. The HHD selectivity maintained around 74% with increasing H_2 pressure at pH of 3.4 after 1 h (Figure S6, Supporting Information). It is likely that the formation of byproduct humins, an acid catalyzed Aldol-condensation product, depends on the solution acidity and reaction time.[42−44] To measure the maximum TOF, we further lowered the concentration of Cp*Ir-L4 to 0.00083 mol %. The TOF peaked at 35 bar of H_2 with an extraordinary TOF of 31 560 h^{-1}. This represents nearly 180-fold increase over that of the best reported data.[7] Further, both HHD selectivity and 5-HMF conversion were

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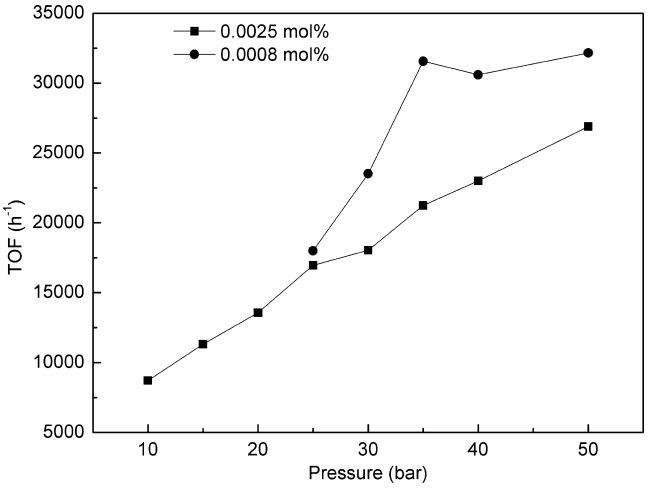


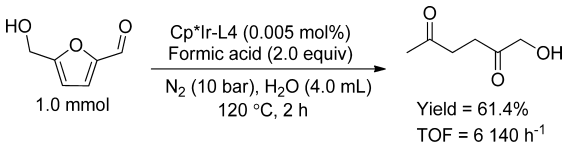
Figure 2. Pressure impacts on the TOF. Reaction conditions: 5-HMF (1.0 mmol), catalyst Cp*Ir-L4 (0.0025 or 0.00083 mol % to 5-HMF), and aqueous solution (pH = 3.4, 4.0 mL), under H_2, at 120 °C, for 1 h. GC-MS yield, *N,N*-dimethylformamide was the internal standard.

monitored as a function of reaction time over Cp*Ir-L4 (0.00083 mol %) under 35 bar H_2 (Figure S7, Supporting Information). The maximum conversion reached near 88%, with the HHD selectivity was near 67% after 6 h. Finally, Cp*Ir-L4 reached an extreme turnover number (TON) of 70 800.

We propose a mechanism of Cp*Ir complex catalyzed H_2 heterolytic dissociation as shown in Scheme 5. Cp*Ir-L4 first releases a proton. A and A′ should be the stable resonance structures.[24,26] H_2 may be activated by A to form B_H through a water bridge pathway.[32] B_H reacts with aldehyde (Scheme 4, step a) or olefin (Scheme 4, step c) to form corresponding products through an 8-membered transition state C,[37,38] and regenerates A′ to undergo the next catalytic cycle. We studied Cp*Ir-L4 and Cp*Ir-L2 catalyzed hydrogenation of furfural in D_2O (details are shown in Table S1 and Scheme S2, Supporting Information). According to the GC-MS analysis of deuterated product furfuryl alcohol, we observed that the hydride/deuteride exchange process (Scheme 5, B_H to B_D) happened during the reaction. Either a Ir(I) intermediate[7,45−47] or a Ir(III) intermediate may be involved in this hydride/deuteride exchange (Scheme S3, Supporting Information). Compared with the electron-withdrawing ligand, the electron-donating ligand may facilitate the cleavage of Ir(III)-H bond to form Ir(III) intermediate and hydride. As Cp*Ir-L2 with an electron-withdrawing group CF_3 resulted a low fraction of B_D intermediate (17% of Ir-D), while Cp*Ir-L4 with an electron-donating group NMe_2 achieved a high fraction of B_D intermediate (28% of Ir-D). The hydride/deuteride exchange is probably through a Ir(III) intermediate.

We further used formic acid as a hydrogenation resource to study Cp*Ir-L4 catalyzed hydrogenation/hydrolysis reaction of 5-HMF (Scheme 6). The 5-HMF conversion reached to 99%

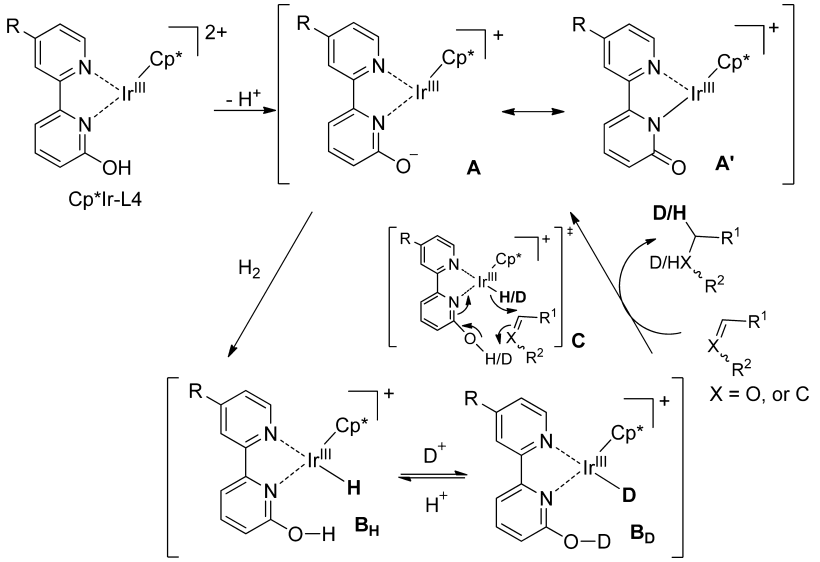
Scheme 6. Synthesis of HHD in the Presence of Formic Acid



after 2 h, and a HHD yield of 61.4% was obtained with only 2 equiv of formic acid in water. Cp*Ir-L4 achieved a TOF of 6140 h^{-1}, which is almost 3 000-fold over the reported method.[15]

In conclusion, we have synthesized highly efficient Cp*Ir catalysts based on a hypothesized design strategy for the hydrogenation/hydrolysis ring opening reaction of 5-HMF to produce diketone HHD. The Cp*Ir-L4 catalyst with both ortho-hydroxyl and strong electron-donating NMe_2 groups achieved the highest TOF (31 560 h^{-1}) and TON (70 800). The Cp*Ir-L4 catalyst also achieved a super high TOF (6140 h^{-1}) by hydrogenation with formic acid. The Cp*Ir-L4 catalyzed H_2 heterolytic dissociation may proceed through a water bridge transition state. The mechanistic study based on the results of GC-MS analysis and statistical calculation showed that the electron-donating ligand L4 promoted the hydride/deuteride exchange process and achieved a higher fraction of Ir-

Scheme 5. Proposed Mechanism



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D intermediate. This work demonstrates a catalyst design strategy for Cp*Ir complex catalyzed heterolytic hydrogenation under acidic conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00826.

Full experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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