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Linear-Organic-Polymer-Supported Iridium Complex as a Recyclable Auto-Tandem Catalyst for the Synthesis of Quinazolinones via Selective Hydration/Acceptorless Dehydrogenative Coupling from *o*-Aminobenzonitriles

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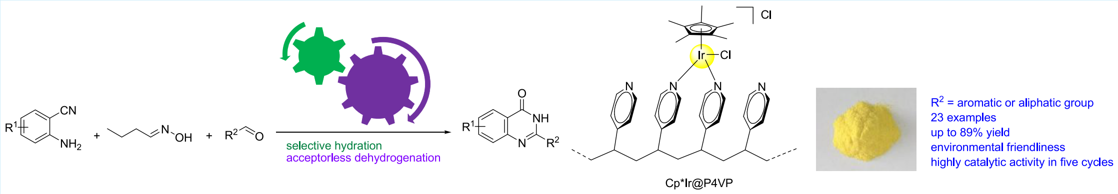

ABSTRACT: A linear-organic-polymer-supported iridium complex Cp*Ir@P4VP, which is designed and synthesized by the coordinative immobilization of $[Cp^*IrCl_2]_2$ on poly(4-vinylpyridine), was proven to be an efficient heterogeneous autotandem catalyst for synthesizing quinazolinones via selective hydration/acceptorless dehydrogenative coupling from *o*-aminobenzonitriles. Furthermore, the synthesized catalyst was recycled five times without an obvious decrease in the catalytic activity.

Quinazolinones, a class of fused heterocyclic compounds, widely occur in various natural alkaloids.[1] They also exhibit remarkable pharmacological and biological properties. Recent instances include their use as antileishmanial agents,[2a] highly active *Clostridium difficile* inhibitors,[2b] dual PI3K/HDAC inhibitors,[2c] and methicillin-resistant *Staphylococcus aureus* (MRSA) inhibitors.[2d] Although many synthetic methods for the construction of quinazolines have been reported in the past few decades, the most general routes rely on the oxidation of aminal intermediates, which are generated by the condensation between aldehydes and *o*-aminobenzamides. However, these methodologies require the use of an excess amount of hazardous or toxic oxidants, such as *t*-BuOOH,[3a] DDQ,[3b] PhI(OAc)$_2$,[3c] MnO$_2$,[3d] KMnO$_4$,[3e] CuCl,[3f] and I$_2$,[3g] and the generation of a large amount of unavoidable byproducts. Moreover, most *o*-aminobenzamides are commercially unavailable and are generally synthesized by the acid- or base-mediated hydration of *o*-aminobenzonitriles under harsh conditions.

In recent years, extensive attention has been paid to acceptorless dehydrogenative reactions, such as the dehydrogenation of alcohols,[4] N-containing heterocycles,[5] and other compounds.[6] Such methodologies represent some of the most atom-economical and clearest processes as alternatives to traditional oxidation. Several groups have also demonstrated transition-metal-catalyzed acceptorless dehydrogenative couplings of *o*-aminobenzamides with aldehydes or alcohols for the synthesis of quinazolinones.[7] We have also demonstrated an efficient strategy for the direct preparation of quinazolinones via iridium-catalyzed one-pot sequential selective hydration/acceptorless dehydrogenation from *o*-aminobenzonitriles.[8] This protocol is highly attractive due to its high atom economy, readily available raw materials, and minimal consumption of energy and chemicals. However, the practical application of this procedure is still highly limited because the catalyst could not be recycled. In addition, this procedure was carried out by the step-by-step addition of raw materials.

Linear-organic-polymer-supported metal complexes have been widely applied in sensors,[9] electrochromic materials,[10] electroluminescence,[11] magnetic materials,[12] organic semiconductors,[13] and cathode interlayers;[14] however, their utilization as heterogeneous autotandem catalysts, which could activate multiple and mechanistically distinct reactions in a single reactor,[15] has remained unexplored due to the fact that compared with inorganic and inorganic/organic hybrid materials, linear organic polymers usually show low thermal stability and chemical resistance at high temperature, which easily causes severe leaching and the deactivation of catalysts.[16]

With continuing interest in the iridium-catalyzed hydrogen autotransfer process[17] and acceptorless dehydrogenative transformations,[18] we turned our attention from homogeneous

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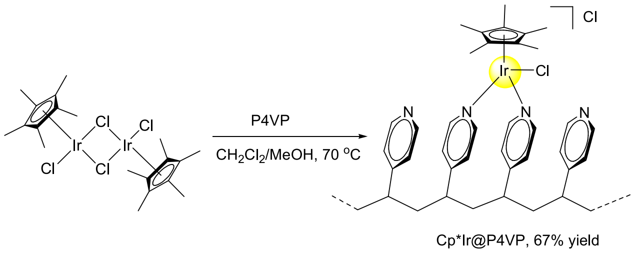
catalysis to heterogeneous catalysis. Herein we report the synthesis and characterization of a linear-organic-polymer-supported iridium complex and its development as a recyclable heterogeneous autotandem catalyst for the synthesis of quinazolinones via selective hydration/acceptorless dehydrogenative coupling from *o*-aminobenzonitriles.

The designed linear-organic-polymer-supported iridium complex Cp*Ir@P4VP was synthesized by the reaction of poly(4-vinylpyridine) (P4VP) and $[Cp^*IrCl_2]_2$ in a mixture of methanol and dichloromethane (v/v = 1/1) at 70 °C for 12 h (Scheme 1). Then, the resulting yellow precipitate was filtered, washed with dichloromethane, and vacuum-dried at 25 °C for 36 h. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images revealed that the mashed Cp*Ir@P4VP is of irregular morphology (Figure 1a,b and Figures S1 and S2). Energy-dispersive X-ray spectroscopy (EDS) mapping indicated that iridium and chloride elements were nearly homogeneously dispersed in the solid matrixes (Figure 1c,d and Figure S3). The actual loading amount of Ir on P4VP was incorporated to be 3.84 wt % by inductively coupled plasma mass spectrometry (ICP-MS) analysis. To elucidate the coordination environment of the iridium cation, an X-ray photoelectron spectroscopy (XPS) measurement was undertaken with the C 1s value (284.6 eV) as a reference (Figure 2). The Ir $4f_{7/2}$ electron-binding energy (EBE) was confirmed to be 62.1 eV, which is 0.6 eV lower than that of $IrCl_3$ (62.7 eV) (Figure 2).[19] This indicates that Cp* and N^N ligands donated electron density to the iridium cation. For comparison, the homogeneous catalyst [Cp*Ir(bpy)Cl]Cl was then analyzed. Its Ir $4f_{7/2}$ EBE value was found to be 62.1 eV, which well matches that of Cp*Ir@P4VP, indicating that the coordination environments of the iridium centers in both complexes are similar (Figures S5 and S6).

Scheme 1. Synthetic Route for Cp*Ir@P4VP



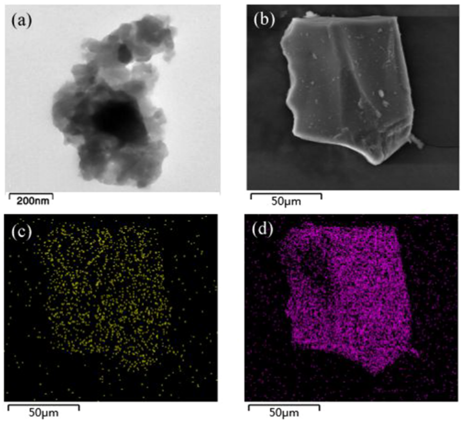


Figure 1. (a) TEM image of Cp*Ir@P4VP. (b) SEM images of Cp*Ir@P4VP. EDS mapping of (c) Ir and (d) Cl.

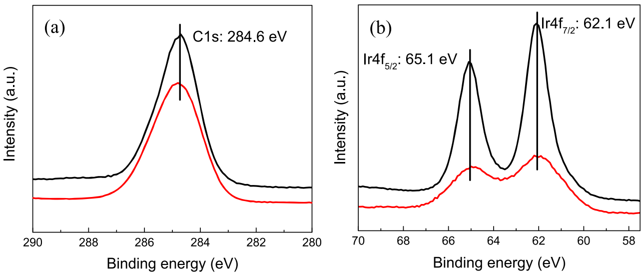
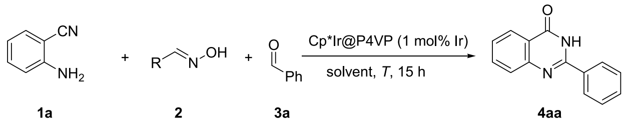


Figure 2. Deconvoluted X-ray photoelectron spectra of (a) C-1s and (b) Ir-4f of Cp*Ir@P4VP (red) and [Cp*Ir(bpy)Cl]Cl (black).

With the synthesized Cp*Ir@P4VP in hand, we screened its ability as an autotandem catalyst for the synthesis of quinazolinones. In the presence of Cp*Ir@P4VP (1 mol % Ir), the coupling of *o*-aminobenzonitrile (**1a**), *n*-butylaldoxime (**2a**) (1.2 equiv), and benzylaldehyde (**3a**) (1.2 equiv) proceeded in *tert*-amyl alcohol at 110 °C for 15 h to afford the desired product **4aa** in 80% yield (Table 1, entry 1). The yield of **4aa** was improved to 93% as the reaction temperature was enhanced to 125 °C (Table 1, entry 2). When 1,4-dioxane, THF, 2-MeTHF, and toluene were used as alternative solvents, the reaction gave the product **4aa** in 43−87% yields (Table 1, entries 3−6). With the use of acetyloxime (**2b**) as a water source, product **4aa** could be obtained in 86% yield (Table 1, entry 7).

Table 1. Synthesis of Quinazolinone from *o*-Aminobenzonitrile Catalyzed by Cp*Ir@P4VP under Various Conditions[a]

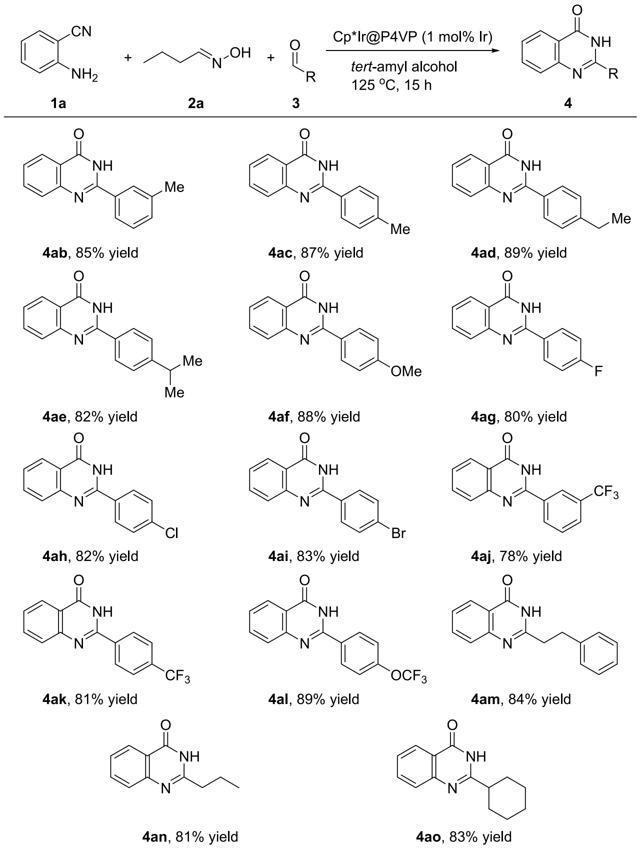


entry	R	*T* (°C)	solvent	yield (%)[b]
1	$-CH_2CH_2CH_3$	110	*tert*-amyl alcohol	80
2	$-CH_2CH_2CH_3$	125	*tert*-amyl alcohol	93 (88%)[c]
3	$-CH_2CH_2CH_3$	125	1,4-dioxane	55
4	$-CH_2CH_2CH_3$	125	THF	46
5	$-CH_2CH_2CH_3$	125	2-MeTHF	43
6	$-CH_2CH_2CH_3$	125	toluene	87
7	$-CH_3$	125	*tert*-amyl alcohol	86

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), **3a** (0.6 mmol), Cp*Ir@P4VP (1 mol % Ir), solvent (2 mL), 15 h. [b] Yield was determined based on the ^1H NMR spectrum of the crude reaction mixture. [c] Isolated yield.

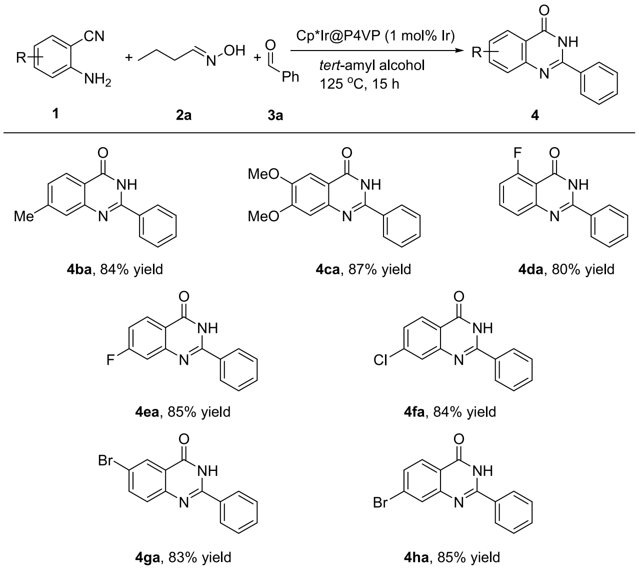
Encouraged by the promising result (Table 1, entry 2), reactions with a variety of aldehydes were examined, and these results are outlined in Scheme 2. Transformations of benzaldehydes bearing an electron-rich substituent afforded the desired products **4ab**−**4af** in 82−89% yields. Similarly, benzaldehydes bearing a halogen atom were cyclized to the corresponding products **4ag**−**4ai** in 80−83% yields. Trifluoromethyl and trifluoromethoxy groups were tolerated, and the desired products **4aj**−**4al** were obtained in 78−89% yields. The system is also compatible with aliphatic aldehydes, including phenylpropylaldehyde, butyraldehyde, and cyclo-

Scheme 2. Scope of Reaction with Respect to Aldehydes Catalyzed by Cp*Ir@P4VP[a,b]



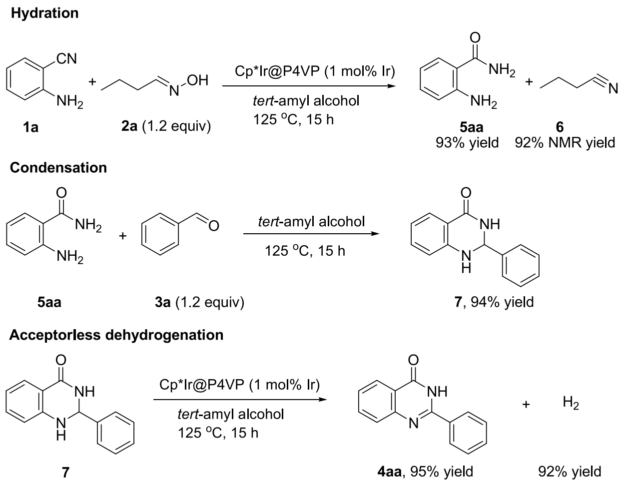
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), 3 (0.6 mmol), Cp*Ir@P4VP (1 mol % Ir), *tert*-amyl alcohol (2 mL), 125 °C, 15 h. [b]Isolated yield.

Scheme 3. Scope of the Reaction with Respect to *o*-Aminobenzonitriles Catalyzed by Cp*Ir@P4VP[a,b]



[a]Reactions conditions: **1** (0.5 mmol), **2a** (0.6 mmol), **3a** (0.6 mmol), Cp*Ir@P4VP (1 mol % Ir), *tert*-amyl alcohol (2 mL), 125 °C, 15 h. [b]Isolated yield.

Scheme 4. Mechanistic Experiments



hexanecarbaldehyde, affording the corresponding products **4am**−**4ao** in 81−84% yields.

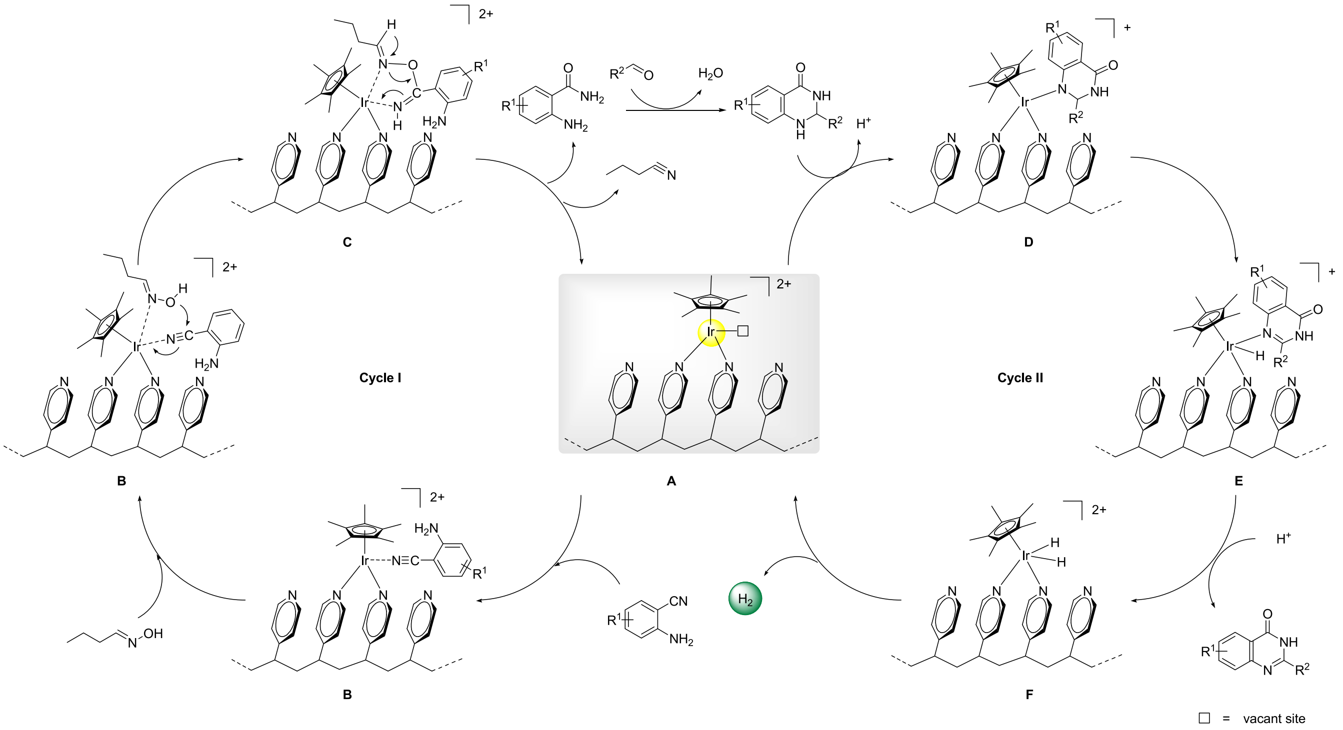
Furthermore, couplings with a series of *o*-aminobenzonitriles were then investigated (Scheme 3). Cyclizations of *o*-aminobenzonitriles bearing one or two electron-donating substituents afforded products **4ba** and **4ca** in 84 and 87% yields, respectively. In the case of substrates with an electron-withdrawing substituent, products **4da**−**4ha** were also isolated in 80−85% yields.

To gain information on the reaction, several mechanistic experiments were undertaken (Scheme 4). In the presence of Cp*Ir@P4VP (1 mol % Ir), the hydration of **1a** with **2a** was carried out at 125 °C for 15 h to afford product **5aa** in 93% yield. In addition, *n*-butyronitrile (**6**) was generated in 92% yield as a byproduct. Then, the condensation between **5aa** and **3a** was performed for 15 h to afford 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**7**) in 94% yield. Under standard conditions, the reaction of **7** proceeded for 15 h to give the product **4aa** in 95% yield with hydrogen gas in 92% yield collected by a water displacement.

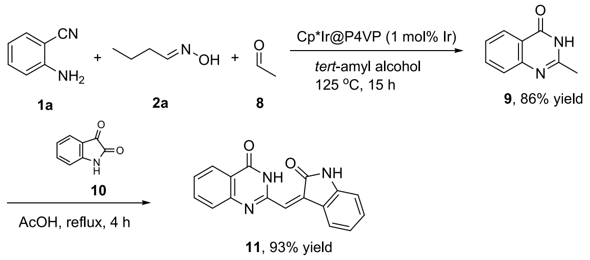
On the basis of previous reports[20,21] and experimental results, a proposed reaction mechanism is shown in Scheme 5. In cycle I, a cationic unsaturated iridium species **A**@P4VP, which is formed by the dissociation of a chloride ion from Cp*Ir@P4VP, was converted to the iridium nitrile species **B**@P4VP through the coordination with *o*-aminobenzonitriles. Furthermore, *n*-butylaldoxime attacked iridium nitrile species **B**@P4VP to form the five-membered cyclic iridium species **C**@P4VP. With the decomposition of species **C**@P4VP, *o*-aminobenzamides were released, and the catalytically active species **A**@P4VP was regenerated. Furthermore, the condensation between aldehydes and the resulting *o*-aminobenzamides gave 2,3-dihydroquinazolinones. In cycle II, 2,3-dihydroquinazolinones were deprotonated and coordinated to the unsaturated iridium species **A**@P4VP, which resulted in the formation of iridium species **D**@P4VP. Then, the *β*-hydrogen elimination of iridium species **D**@P4VP afforded iridium species **E**@P4VP, which underwent protonation to give iridium dihydride species **F**@P4VP and quinazolinones as desirable products. Finally, hydrogen gas was liberated from iridium dihydride species **F**@P4VP, and the catalytically active species **A**@P4VP was regenerated.

Furthermore, the gram-scale synthesis of a natural alkaloid Schizocommunin[22] was represented (Scheme 6). Under standard conditions (Table 1, entry 2), the coupling of **1a**

Scheme 5. Proposed Reaction Mechanism



Scheme 6. Gram-Scale Synthesis of a Natural Alkaloid Schizocommunin



(2.36 g, 20 mmol), **2a** (2.09 g, 24 mmol), and acetaldehyde **8** (1.06 g, 24 mmol) was performed to afford the key intermediate **9** in 86% yield. Subsequently, the reaction of **9** and isatin **10** proceeded in AcOH under reflux for 4 h to give the desirable product **11** in 93% yield as a single diastereomer.

The recyclability of the catalyst for the model reaction was then investigated (Figure 3). After each recycling, the catalyst was recovered by filtration, washed with a small amount of methanol, and applied to the next cycle. The activity of the catalyst was well maintained during the recycling experiments, and the NMR yield of **4aa** was still up to 85% in the fifth cycle. Furthermore, the recovered catalyst after the fifth cycle was analyzed. The TEM and SEM images and EDS mapping showed that the original morphology and the homogeneous distribution of the Ir element in P4VP were maintained (Figures S1, S2, and S4). SEM−EDS analysis also showed that the Ir content of the recovered catalyst was slightly lower than that of the fresh catalyst (Table S1).

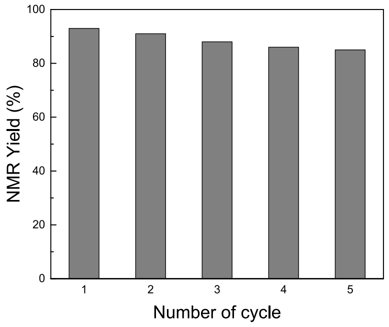


Figure 3. Recyclability of Cp*Ir@P4VP for the model reaction.

In conclusion, we have demonstrated the synthesis and characterization of a linear polymer-supported iridium complex Cp*Ir@P4VP by the coordinative immobilization of $[Cp^*IrCl_2]_2$ on poly(4-vinylpyridine). Furthermore, this complex was proven to be an efficient heterogeneous autotandem catalyst for the synthesis of quinazolinones from *o*-aminobenzonitriles. Furthermore, the synthesized catalyst was recycled five times without an obvious decrease in catalytic activity. Notably, this study exhibits the potential of linear polymer-supported metal complexes as heterogeneous autotandem catalysts for organic synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00475.

Experimental procedures and characterization data (PDF)

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[†]S.H. and J.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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