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Metal-Free Photoredox Intramolecular Cyclization of N-Aryl Acrylamides

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Abstract: A novel metal-free photoredox-catalyzed cyclization reaction of *N*-aryl acrylamide is herein reported that provides synthetically valuable oxindole derivatives through the bis-mediation of H_2O and aldehyde. In this work, sustainable visible light was used as the energy source, and the organic light-emitting molecule 4CzIPN served as the efficient photocatalyst. The main characteristics of this reaction are environmentally friendly and high yields.

Keywords: radical cyclization; hydroarylation; oxindoles; visible-light

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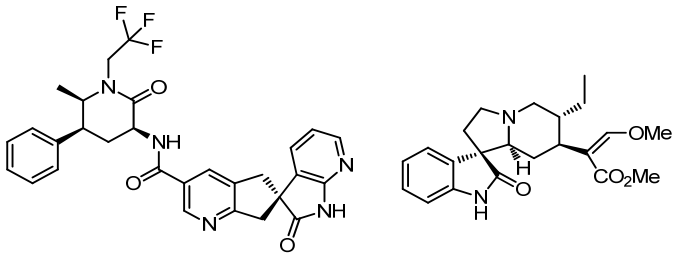
1. Introduction

Oxindole is a highly important skeleton that widely exists in biologically active compounds such as naturally occurring products [1] and drugs [2]. Specifically, oxindole compounds represent an important class of drugs with antibiotic, anticancer, antiviral, and other activities [3–5]. For example, ubrogepant [6], a drug for the treatment of migraine, contains a 3-cyclopentyl spiro-7-azaoxindole core. Rhynchophylline [7], which inhibits the activity of peripheral vascular contraction, could reduce vascular resistance and blood pressure and have the effect of anti-platelet aggregation and anti-thrombus (Figure 1).



Ubrogepant **Rhynchophylline**

Figure 1. Bioactive molecules containing the oxindole motif.

Because of the pharmaceutical significance of oxindoles [8–10], the construction of this motif has attracted considerable attention among synthetic chemists [11–13]. In the past few years, many functional groups have been installed successfully to oxindoles through the treatment of NBS [14], AgSCN [15], 2,4-pentanedione [16], and AIBN [17]. However, these strategies required stoichiometric amounts of functionalized reagents, high metal catalyst loading, strong oxidant and elevated temperature for high reaction efficiency. On the other hand, as one of the most attractive topics in organic chemistry, hydroarylation process has drawn interest of chemists in the past decades [18–24]. Recently, Pan and our group [25,26] independently reported a visible-light-induced hydrocyclization of unactivated alkenes

which generated the polycyclic quinazolinones. (Figure 2a). Photochemical radical addition and cyclization of *N*-arylacrylamide provide reliable access to a range of functionalized oxindoles [27–37]. Alternatively, our group reported visible light-induced photocatalytic systems for intramolecular hydroarylation of *N*-arylacrylamide by proton-coupled electron transfer (PCET) process [38] and energy transfer [39] (Figure 2b). However, this reaction requires the addition of strong acids and chlorobenzene as reaction solvent, which limits the substrate scope and further synthetic application. Inspired by these cyclizations of alkene studies, we envision an acid-free visible-light-mediated photocyclization strategy from *N*-aryl acrylamide to access oxindole skeletons. (Figure 2c). In our recent findings of redox-neutral radical addition and cyclization of *N*-arylacrylamides with benzaldehydes [40], aliphatic aldehydes did not proceed through the coupling, probably because of the higher reductive potential of them than aromatic aldehydes [41]. Instead, the hydroarylation oxindole product was accessed in moderate yield when pivalaldehyde was exploited in this system. This result encouraged us to explore an acid-free hydroarylation process of N-aryl acrylamide, which was herein reported.

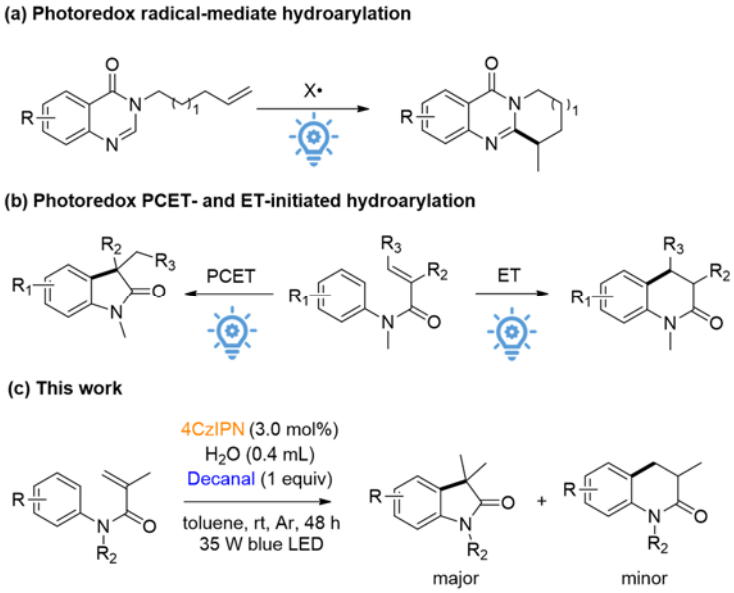


Figure 2. Cyclization and hydroarylation methods.

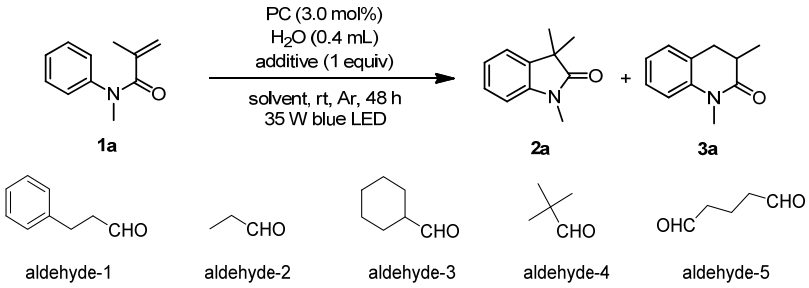
2. Results and Discussion

Therefore, the optimization studies were performed by selecting *N*-methly-*N*-phenylmethacrylamide (**1a**) as the standard reactant. Initially, when the cyclization reaction was performed using 4CzIPN as photocatalyst (PC) along with decanal as additive in water/toluene mixed solvent under a 36 W blue LED at argon atmosphere (Table 1, entry 1), the desired product **2a** was obtained in 80% yield. Then, this reaction was independently conducted in the absence of light irradiation (Table 1, entry 2, 0%), water (Table 1, entry 3, yield 17%), PC (Table 1, entry 4, 0%) and aldehydes (Table 1, entry 5, 0%). These control experiments demonstrated the critical role of visible light, photocatalyst and aldehyde and the promotional effect of H_2O. We next moved on to screen photocatalysts include Rose bengal (Table 1, entry 6), $Mes_2AcrtBu_2BF_4$ (Table 1, entry 7), Xanthone (Table 1, entry 8), and 9-Fluorenone (Table 1, entry 9), and found that those PCs were all ineffective. However, neutral Eosin Y showed also a good efficiency (Table 1, entry 10, yield 73%). Other solvents such as THF, DMF, EtOAc, NMP and CH_3CN (Table 1, entry 11–16) were investigated, all of which showed inferior results as compared with toluene. PhCl (Table 1, entry 17) and *o*-Xylene (Table 1, entry 18) showed moderate yields (65% and 70% yields, respectively). Furthermore, the screening of other aldehyde additives such as 3-phenylpropanal, propionaldehyde, cyclohexanecarbaldehyde, pivalaldehyde, and glutaraldehyde, afforded the cyclization product with slightly reduced yields (Table 1,

entries 19–23). Finally, decreasing the photocatalyst loading to 2 mol% resulted in 60% yield of products, with significant amounts of **1a** remained (Table 1, entry 24).

Table 1. Optimization of Reaction Conditions [a].

Entry	PC	Additive	Solvent	Yield of 2a (%) [b]
1	4CzIPN	Decanal	toluene	80
2 [c]	4CzIPN	Decanal	toluene	NR
3 [d]	4CzIPN	Decanal	toluene	17
4	-	Decanal	toluene	NR
5	4CzIPN	-	toluene	NR
6	Rose bengal	Decanal	toluene	NR
7	$Mes_2AcrtBu_2PF_6$	Decanal	toluene	NR
8	Xanthone	Decanal	toluene	NR
9	9-Fluorenone	Decanal	toluene	NR
10	Eosin Y	Decanal	toluene	73
11	4CzIPN	Decanal	THF	NR
12	4CzIPN	Decanal	DMF	NR
13	4CzIPN	Decanal	EtOAc	NR
14	4CzIPN	Decanal	DCE	NR
15	4CzIPN	Decanal	NMP	NR
16	4CzIPN	Decanal	CH_3CN	NR
17	4CzIPN	Decanal	PhCl	65
18	4CzIPN	Decanal	o-Xylene	70
19	4CzIPN	Aldehyde-1	toluene	40
20	4CzIPN	Aldehyde-2	toluene	67
21	4CzIPN	Aldehyde-3	toluene	33
22	4CzIPN	Aldehyde-4	toluene	57
23	4CzIPN	Aldehyde-5	toluene	61
24 [e]	4CzIPN	Decanal	toluene	60



[a] Reaction conditions: **1a** (35 mg, 0.2 mmol), additive (0.2 mmol, 1 equiv), photocatalyst (0.006 mmol), H_2O (0.4 mL), solvent (1 mL), under Ar atmosphere, using 35 W blue LED. [b] Isolated yield of **2a** was given, and regioselective ratio of **2a**/**3a** was more than 25/1 in all cases in this table. [c] In dark. [d] No water. [e] 4CzIPN (2 mol%, 0.004 mmol) was used.

With the optimized reaction condition in hand, we next explored the substrate scope of the photocyclization reaction of *N*-arylacrylamides (Figure 3). Generally, a broad range of *N*-arylacrylamides with various functional groups were subjected and found compatible with this system. The halo-substituted *N*-methyl-*N*-phenylmethacrylamides were carried out with the photochemical reaction, leading to the corresponding halo-substituted (such as -Cl, -Br, -I) oxindoles in moderate yields (Figure 3, **2b**, **2c**, **2d**, 35–45% yields), along with the formation of the dihydroquinolines in a trace amount. When alkyl groups such as methyl and tert-butyl were attached, the cyclization products were obtained in excellent yields (Figure 3, **2e–2h**, yields 74–89%). As a comparison, para-, meta-, and ortho- substituted compounds were successfully tested and the position of these substituents had little impact on the yield. Notably, meta-substituted *N*-aryl acrylamide was viable under standard conditions to give the desired product with poor regioselectivity (**2g**). Introducing a benzyl substituent in the α-position of acrylamides did not have obviously deleterious effects on the reaction yield (**2i**, 85% yield). The reactants with various *N*-protecting functional groups including phenyl, ethyl, isopropyl and cyclohexyl generated the corresponding

products in generally good yields (**2j**, 90% yield, **2l**, 82% yield, **2m**, 78% yield, **2o**, 83% yield). The benzyl protective group (**2k**) is well tolerated with 70% yield, which could be converted to NH oxindole by debenzylation. In addition, the reaction was extended to phenyl ether, leading to **2n** in a modest yield. Then, the reaction systems were found to tolerate the substrate attached with drug molecule such as naproxen (**2p**, 72% yield). Cyclic and diaryl *N*-acylamines were exploited to smoothly produce the polycyclic products (**2q–2s**) and *N*-aryl oxindoles (**2q**) with yield ranging from 65% to 73%. While our 4CzIPN/decanal catalytic system enabled exclusive 5-exo-trig selectivity for most of the above reactants, *N*-methyl-*N*-arylcinnamamides (**1t**) afforded the corresponding 4-arylquinolinone as the major product (**3t**, 83%). When the reactants contain strong electron-absorbing groups and partial non-terminal alkenyl, the reaction cannot be performed effectively (See Supplementary Materials for details).

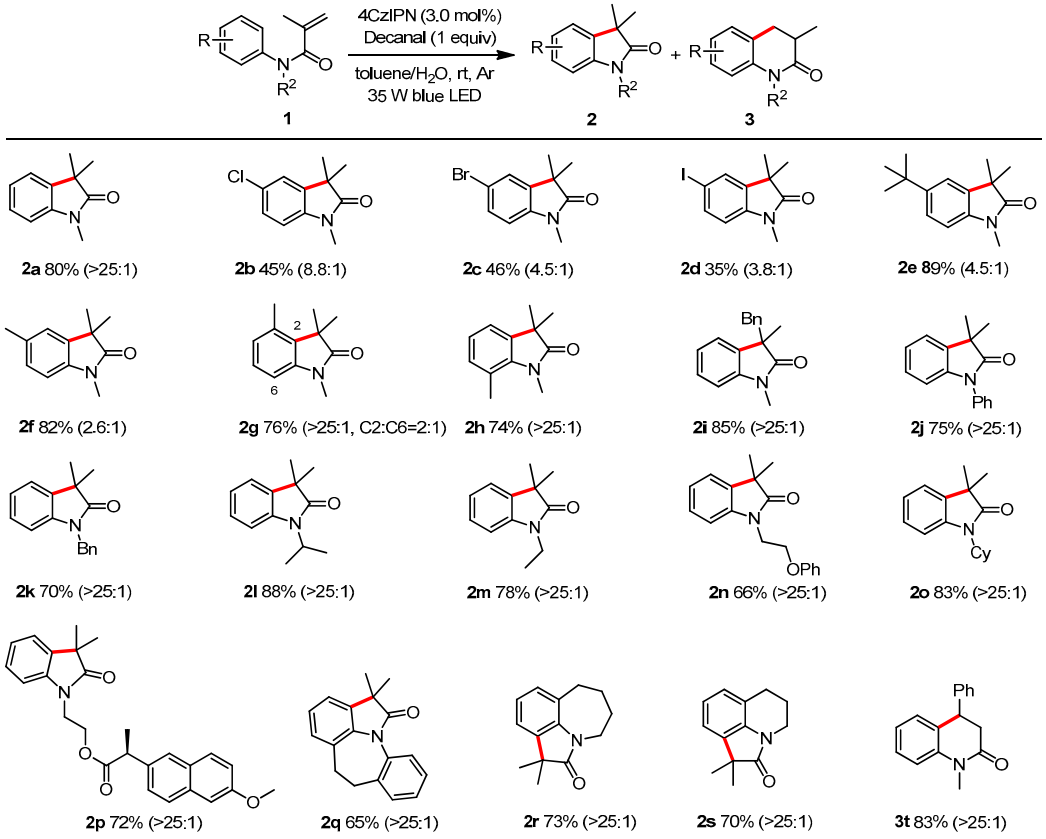


Figure 3. Substrate scope of photocyclization of *N*-arylacrylamides.

Because of the superior electrocyclization reactivity, the π-extension substrates such as biphenyl acrylamide (**1u**) and *N*-(4-methoxyphenyl)-*N*-methylmethacrylamide (**1v**) led to the formation of 3,4-dihydroquinolinones as the major products in the current systems (**3u** and **3v**). Besides, we changed the equivalent amounts of the decanal to explore the site-selectivity control for 6-endo-trig vs. 5-exo-trig cyclization of *N*-([1,1′-biphenyl]-4-yl)-*N*-methylmethacrylamide. While exclusive 6-endo-trig selectivity was observed in the absence of aldehyde additives, the 5-exo-trig cyclization process was enhanced when increasing the amount of decanal (Figure 4). The results indicate that the addition of aldehyde additives in the systems could alter the reaction pathways over 5-exo-trig cyclization.

Next, control experiments were conducted to gain mechanistic insights into the present aldehyde-promoted hydroarylation reaction (Scheme 1). The addition of the radical scavenger 2,2,6,6- tetramethylpiperidin-1-oxyl (TEMPO) or 1,1-diphenylethylene (DPE) to the standard conditions caused complete quenching in the yield of **2a** (Scheme 1a). The H/D exchange experiments show that when D_5-labeled *N*-acylaniline (D_5-**1a**) was used, no D incorporation of cyclized products was observed. Comparably, the addition of D_2O led to 83%

incorporation of D into newly formed methyl groups (Scheme 1b), indicating the hydrogen in the reaction being derived from water. The control experiment with 3-phenylpropanal under the standard conditions within 24 h furnished the oxindole product **2a** in 59% yield, along with the detection of both 3-phenylpropanoic acid and 3-phenylpropan-1-ol. This result suggests the by-product formation from aliphatic aldehyde. The Stern−Volmer quenching experiments indicate that while the acrylamide **1a** had not fluorescence quenching effect, the decanal additive quenched slightly the fluorescence emission of excited 4CzIPN (K_{SV} = 54.9, Scheme 1d). Our previous work had also demonstrated that the substrate **1v** (K_{SV} = 41.3) and **1t** (K_{SV} = 912.4) show also quenching effect, which could be attributed to energy transfer [36]. Finally, the results of the light on/off experiment showed that the present reaction was a continuous illumination reaction (See Supplementary Materials for details).

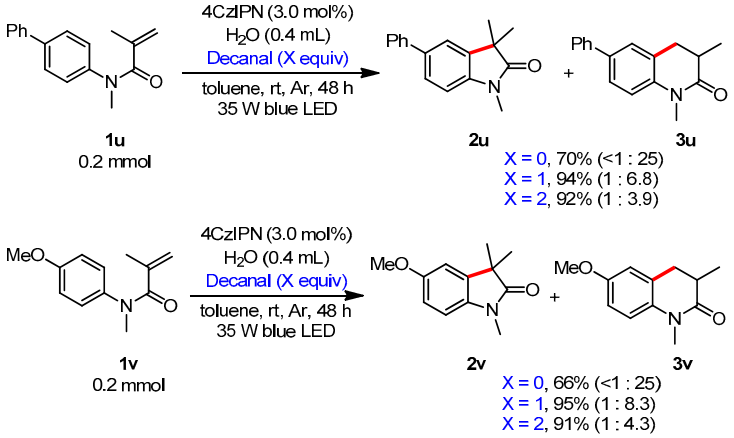
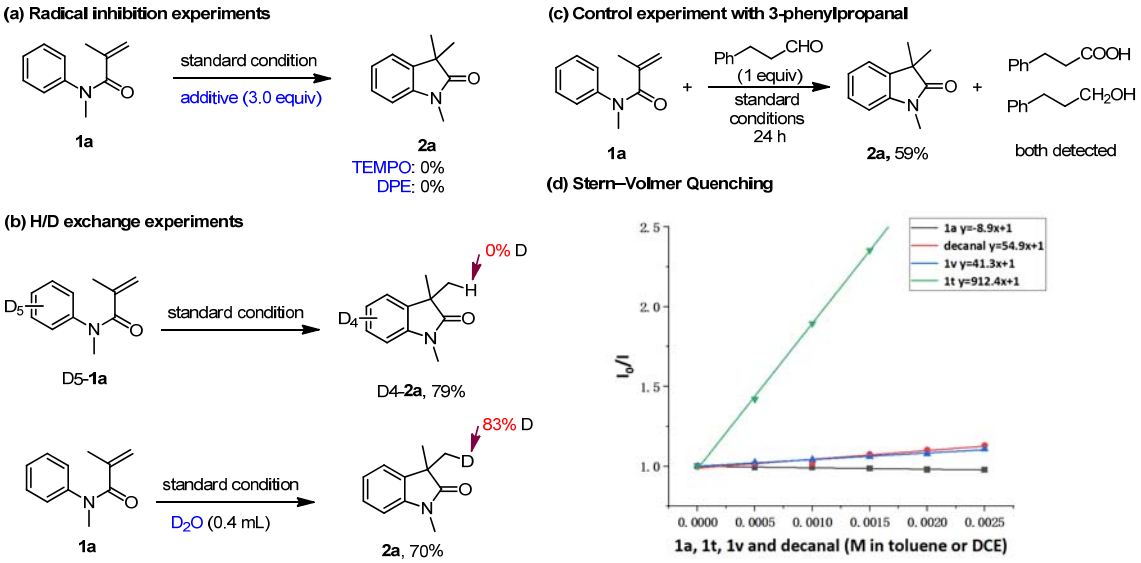


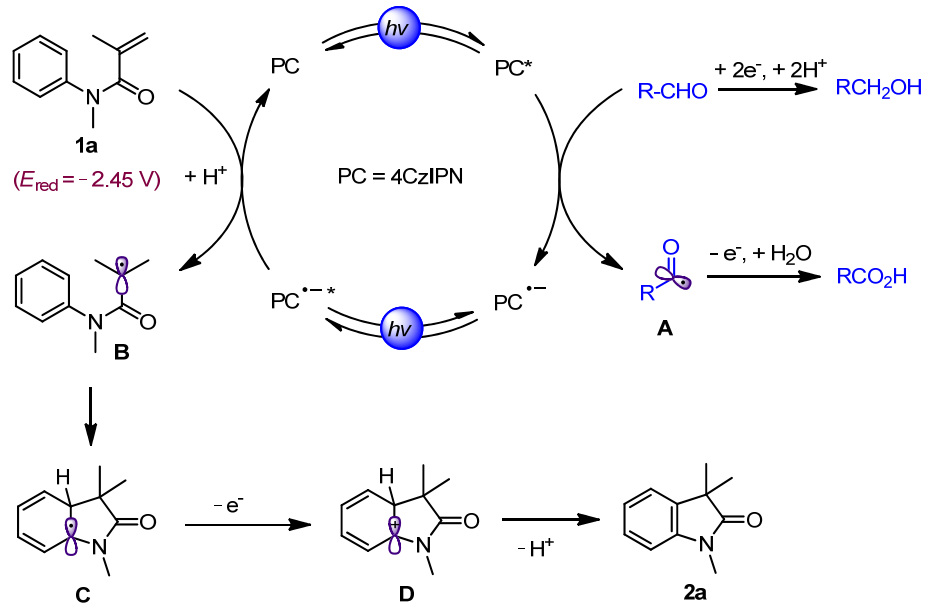
Figure 4. Competitive cyclization.



Scheme 1. Mechanistic studies.

On the basis of above results of mechanistic studies and previous reports, a possible reaction mechanism involving basically consecutive photoinduced electron transfer (ConPET) [40,42] was proposed (Scheme 2). The 4CzIPN photocatalyst absorbs photon to generate its excited state PC*, which oxidize the aldehydes to give PC anion radical and acyl radical **A**. The second irradiation of it occurs to afford the excited state of PC anion radical. This highly reductive species (E_{red} < −2.9 V vs. SCE) [43] undergoes single electron transfer with acrylamide **1a** (E_{red} = −2.45 V vs. SCE) with the assistance of proton

to produce the radical species **B**. The subsequent intramolecular radical cyclization, single electron transfer, and deprotonation sequentially proceed to afford the final product **2a**. The formation of 3-phenylpropanoic acid and 3-phenylpropan-1-ol can be attributed to the further oxidization of acyl radical and two electron reduction of aldehyde, respectively. We suspect that aliphatic aldehydes have higher reductive potential so that they are easier to be oxidized by the excited photocatalyst.



Scheme 2. Possible reaction mechanism.

3. Materials and Methods

3.1. Materials and Chemicals

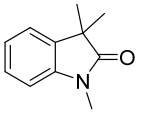
All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. Colum chromatography was performed using silica gel (200–300 mesh) and thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$, acetone-d_6 or dimethyl sulfoxide-d_6 as solvent. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and HRMS data with those of literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Reagents were used as received or prepared in our laboratory.

3.2. General Procedure for Hydroarylation (Standard Conditions)

A 10 mL vial was charged with *N*-methly-*N*-phenylmethacrylamide (1a, 35 mg, 0.2 mmol), 4CzIPN (5 mg, 0.006 mmol), decanal (32 mg, 0.2 mmol), H_2O (0.4 mL), toluene (1 mL). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). The resulting mixture was stirred at 2000 RPM for 48 h under irradiation with a 36 W blue LED. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3 × 20 mL). The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. The reaction yield was quantified by separation, and then column chromatography was performed using silica gel (200–300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **2a**.

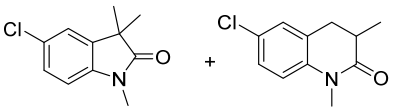
3.3. Characterization Data of Products

1,3,3-trimethylindolin-2-one (2a) [38]



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2a** (28 mg, 80%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29–7.23 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 1.37 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.4, 142.6, 135.8, 127.7, 122.5, 122.3, 108.0, 44.2, 26.23, 24.4.

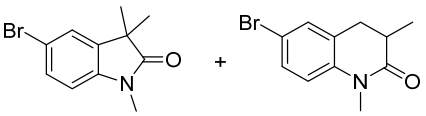
5-chloro-1,3,3-trimethylindolin-2-one (2b) and 6-chloro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (8.8:1) (3b) [38]



(8.8 : 1)

Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield mixture of **2b** and **3b** (19 mg, 45%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.32 (s, 0.3H), 3.20 (s, 3H), 2.90 (dd, *J* = 14.1, 4.3 Hz, 0.16H), 2.76–2.50 (m, 0.32H), 1.36 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.8, 141.2, 137.5, 127.9, 127.6, 122.9, 108.9, 44.5, 26.3, 24.3.

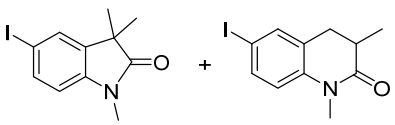
5-bromo-1,3,3-trimethylindolin-2-one (2c) and 6-bromo-1,3-dimethyl-3,4-dihydroquinolin- 2(1*H*)-one (4.5:1) (3c) [38]



(4.5 : 1)

Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield mixture of **2c** and **3c** (23 mg, 46%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 3.33 (s, 0.67H), 3.19 (s, 3H), 2.90 (dd, *J* = 14.3, 4.4 Hz, 0.18H), 2.74–2.56 (m, 0.39H), 1.36 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.7, 141.7, 137.9, 130.5, 130.2, 125.7, 116.1, 115.2, 109.51, 44.4, 35.3, 32.9, 29.9, 26.3, 24.3, 15.7.

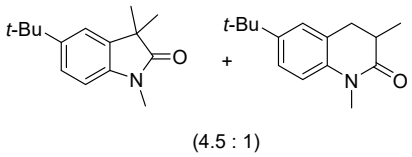
5-iodo-1,3,3-trimethylindolin-2-one (2d) and 6-iodo-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (3.8:1) (3d) [38]



(2.6 : 1)

Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield mixture of **2d** and **3d** (21 mg, 35%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.48 (s, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 3.32 (s, 0.79H), 3.19 (s, 3H), 3.08–2.77 (m, 0.39H), 2.71–2.59 (m, 0.52H), 1.36 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.6, 142.4, 138.3, 136.5, 131.3, 120.4, 116.5, 110.1, 85.7, 85.1, 44.3, 35.3, 32.8, 29.8, 26.3, 24.3, 15.6.

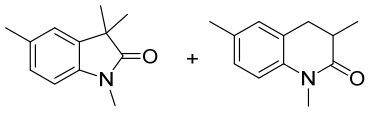
5-(tert-butyl)-1,3,3-trimethylindolin-2-one (2e) and 6-(*tert*-butyl)-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (4.5:1) (3e) [38]



(4.5 : 1)

Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield mixture of **2e** and **3e** (41 mg, 89%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32–7.23 (m, 2H), 6.78 (d, *J* = 8.1 Hz, 1H), 3.35 (s, 0.67H), 3.21 (s, 3H), 2.92 (dd, *J* = 14.5, 4.9 Hz, 0.23H), 2.80–2.40 (m, 0.46H), 1.38 (s, 6H), 1.33 (d, *J* = 6.1 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.8, 140.3, 135.6, 124.2, 119.4, 107.4, 44.4, 34.6, 31.7, 31.4, 26.2, 24.5.

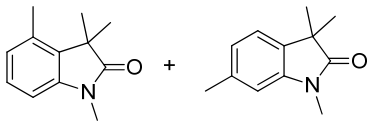
1,3,3,5-tetramethylindolin-2-one (2f) and 1,3,6-trimethyl-3,4-dihydroquinolin-2(1*H*)-one (2.6:1) (3f) [38]



(2.6 : 1)

Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield mixture of **2f** and **3f** (31 mg, 82%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08–7.00 (m, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 3.33 (s, 1.17H), 3.19 (s, 3H), 2.93–2.83 (m, 0.38H), 2.71–2.50 (m, 0.85H), 2.69–2.57 (m, 1H), 2.35 (s, 3H), 2.30 (s, 1.14H), 1.35 (s, 6H), 1.24 (d, *J* = 6.7 Hz, 1.64H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.3, 140.2, 135.8, 132.1, 131.9, 128.6, 127.8, 123.1, 114.3, 107.7, 44.2, 35.5, 33.2, 29.7, 26.2, 24.4, 21.1, 20.5, 15.7.

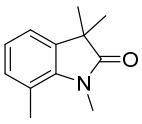
1,3,3,4-tetramethylindolin-2-one (2g) and 1,3,3,6-tetramethylindolin-2-one (2:1) (2g′)[1]



(2 : 1)

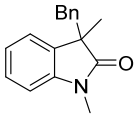
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2g + 2g′** (29 mg, 76%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (t, *J* = 7.6 Hz, 0.68H),7.08 (d, *J* = 7.6 Hz, 0.34H), 6.87 (d, *J* = 7.6 Hz, 0.34H), 6.83 (d, *J* = 7.6 Hz, 0.68H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.20 (s, 3H), 2.40 (s, 2H), 2.39 (s, 1H), 1.45 (s, 4H), 1.35 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.7, 181.4, 142.9, 142.7, 134.1, 133.0, 132.6, 127.5, 125.0, 122.9, 122.0, 109.0, 105.8, 45.0, 44.0, 26.3, 24.5, 22.4, 21.8, 18.1.

1,3,3,7-tetramethylindolin-2-one (2h) [38]



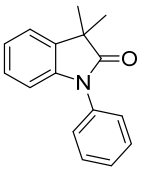
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2h** (28 mg, 74%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.05 (d, *J* = 8.0 Hz, 1H), 6.96 (dt, *J* = 14.7, 7.1 Hz, 2H), 3.50 (s, 3H), 2.59 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.1, 140.4, 136.5, 131.4, 122.4, 120.2, 119.7, 43.5, 29.6, 24.8, 19.1.

3-benzyl-1,3-dimethylindolin-2-one (2i) [38]



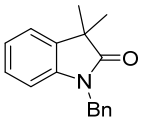
Prepared according to standard conditions within 96 h. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2i** (43 mg, 85%) as a solid. mp: 87–90 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 6.6 Hz, 1H), 7.10–6.98 (m, 4H), 6.85 (dd, *J* = 7.2, 2.1 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 3.12 (d, *J* = 13.0 Hz, 1H), 3.01 (d, *J* = 13.0 Hz, 1H), 2.99 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 143.1, 136.2, 133.0, 129.8, 127.8, 127.5, 126.4, 123.3, 122.1, 107.8, 50.0, 44.6, 25.9, 22.8.

3,3-dimethyl-1-phenylindolin-2-one (2j) [38]



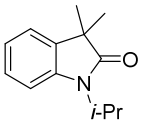
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2j** (36 mg, 75%) as a solid. mp: 84–86 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 7.7 Hz, 2H), 7.44–7.39 (m, 3H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 1.51 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.7, 142.5, 135.7, 134.7, 129.6, 127.9, 127.6, 126.6, 123.0, 109.4, 44.3, 24.8.

1-benzyl-3,3-dimethylindolin-2-one (2k) [38]



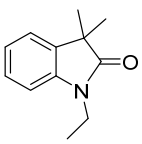
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2k** (35 mg, 70%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33–7.25 (m, 5H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 8.3 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 4.93 (s, 2H), 1.45 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.5, 141.7, 136.1, 135.8, 128.8, 127.6, 127.2, 122.5, 122.4, 109.1, 44.2, 43.6, 24.6.

1-isopropyl-3,3-dimethylindolin-2-one (2l) [38]



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2l** (35 mg, 88%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 2H), 4.71–4.61 (m, 1H), 1.47 (d, *J* = 7.1 Hz, 6H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.1, 136.4, 127.3, 122.5, 121.9, 109.9, 43.8, 43.4, 24.0, 19.4.

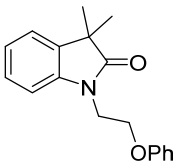
1-ethyl-3,3-dimethylindolin-2-one (2m) [38]



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2m** (29 mg, 78%) as a colorless liquid. ^{1}H NMR

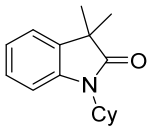
(400 MHz, Chloroform-*d*) δ 7.28–7.18 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.77 (q, *J* = 7.2 Hz, 2H), 1.36 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.9, 141.6, 136.0, 127.5, 122.4, 122.2, 108.1, 44.0, 34.4, 24.3, 12.7.

3,3-dimethyl-1-(2-phenoxyethyl)indolin-2-one (2n) [38]



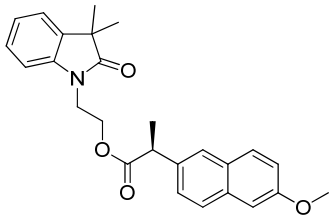
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2n** (37 mg, 66%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31–7.19 (m, 4H), 7.08 (t, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.23 (t, *J* = 5.6 Hz, 2H), 4.14 (t, *J* = 5.6 Hz, 2H), 1.39 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.7, 158.4, 142.2, 135.7, 127.6, 122.5, 122.4, 121.1, 114.5, 109.0, 65.4, 44.1, 24.5.

1-cyclohexyl-3,3-dimethylindolin-2-one (2o) [38]



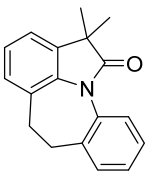
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2o** (40 mg, 83%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25–7.17 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 1H) 7.02 (t, *J* = 7.7 Hz, 1H), 4.24–4.11 (m, 1H), 2.22–2.08 (m, 2H), 1.89 (d, *J* = 13.3 Hz, 2H), 1.80–1.68 (m, 3H), 1.48–1.26 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 141.6, 136.4, 127.3, 122.5, 121.8, 110.1, 51.9, 43.8, 29.2, 26.0, 25.5, 24.6.

2-(3,3-dimethyl-2-oxoindolin-1-yl)ethyl 2-(6-methoxynaphthalen-2-yl)propanoate (2p) [38]



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2q** (60 mg, 72%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67–7.60 (m, 2H), 7.53 (s, 1H), 7.31–7.25 (m, 1H), 7.18–7.07 (m, 4H), 7.02 (t, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 4.41–4.23 (m, 2H), 4.03–3.82 (m, 5H), 3.75 (q, *J* = 7.1 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.31 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.5, 174.5, 157.6, 141.8, 135.7, 135.3, 133.7, 129.3, 127.6, 126.0, 122.5, 122.4, 119.0, 108.4, 105.5, 61.9, 55.4, 45.4, 44.0, 38.9, 18.3.

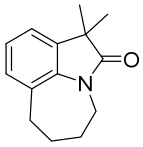
2,2-dimethyl-6,7-dihydrobenzo [6,7]azepino [3,2,1-hi]indol-1(2H)-one (2q) [38]



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2p** (34 mg, 65%) as a solid. mp: 185–188 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.31–7.25 (m, 1H), 7.23–7.14 (m, 2H),

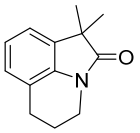
7.12 (dd, *J* = 6.3, 2.2 Hz, 1H), 7.05–6.96 (m, 2H), 3.20–2.92 (m, 4H), 1.49 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.8, 139.7, 136.7, 136.2, 136.1, 129.5, 126.5, 126.3, 126.2, 125.1, 122.4, 120.2, 43.9, 34.0, 33.7, 29.7, 25.2.

7,7-dimethyl-1,2,3,4-tetrahydroazepino [3,2,1-hi]indol-6(7H)-one (2r) [38]



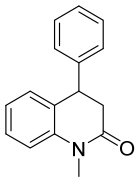
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2r** (31 mg, 73%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.04 (dd, *J* = 6.9, 1.5 Hz, 1H), 6.99–6.90 (m, 2H), 4.03–3.88 (m, 2H), 3.03–2.88 (m, 2H), 2.09–1.95 (m, 4H), 1.36 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.8, 141.3, 136.2, 129.0, 125.2, 122.3, 120.1, 44.2, 40.9, 30.9, 26.5, 26.4, 24.7.

1,1-dimethyl-5,6-dihydro-4H-pyrrolo [3,2,1-ij]quinolin-2(1H)-one (2s) [38]



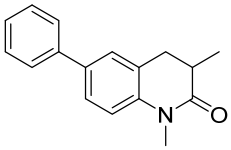
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2s** (28 mg, 70%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06–6.99 (m, 2H), 6.97–6.92 (m, 1H), 3.75–3.69 (m, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.01 (p, *J* = 6.0 Hz, 2H), 1.37 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.3, 138.5, 134.4, 126.4, 121.9, 120.1, 45.6, 38.8, 24.7, 24.2, 21.2.

1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (3t) [39]



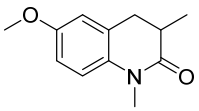
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2t** (39 mg, 83%) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.25 (m, 5H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 1H), 7.03–6.98 (m, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 4.24 (t, *J* = 7.3 Hz, 1H), 3.40 (s, 3H), 3.02–2.90 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 141.0, 140.3, 129.1, 128.8, 128.0, 127.8, 127.7, 127.1, 123.0, 114.8, 41.4, 38.8, 29.5.

1,3-dimethyl-6-phenyl-3,4-dihydroquinolin-2(1H)-one (3u)[39]



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2u** (47 mg, 94%) as a colorless solid.mp: 95–98 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.53–7.39 (m, 5H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 3.40 (s, 3H), 3.26 (s, 0.44H), 3.00 (dd, *J* = 14.8, 5.1 Hz, 0.98H), 2.81–2.62 (m, 2.07H), 1.43 (s, 0.91H), 1.30 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 140.2, 139.6, 135.6, 128.8, 127.1, 126. 7, 126.5, 125.9, 114.8,108.2, 35.5, 33.4, 29.8, 24.4, 15.7.

6-methoxy-1,3-dimethyl-3,4-dihydroquinolin-2(1H)-one (3v)[39]



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **2u** (21 mg, 95%) as a colorless solid.mp: 75–76 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.85 (d, *J* = 8.8 Hz, 1H), 6.75 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.72–6.69 (m, 1H), 3.77 (s, 1H), 3.76 (s, 3H), 3.30 (s, 3H), 3.16 (s, 0.36H), 2.90–2.83 (m, 1H), 2.67–2.54 (m, 2H), 1.34 (s, 0.9H), 1.22 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 155.2, 133.9, 127.1, 115.3, 114.1, 76.9, 55.5, 35.4, 33.5, 29.9, 24.4, 15.6.

4. Conclusions

In summary, we have developed a mild acid- and metal-free photoredox system that enables highly efficient hydroarylation and cyclization of *N*-arylacrylamides. In this system, aliphatic aldehyde was used instead of strong acid and bromide additive which makes it milder and easier to handle and has probably broader potential applications in the synthesis of more complex compounds.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13061007/s1, detailed experiments, mechanistic studies, and NMR spectra of all products.

Author Contributions: Conceptualization, H.H.; experimental investigation, Z.L.; writing—original draft preparation, Z.L. and H.H.; writing—review and editing, X.J., F.Z. and G.D.; supervision, F.Z. and H.H. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings in the work are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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