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Visible-Light-Induced Decarboxylation of Dioxazolones to Phosphinimidic Amides and Ureas

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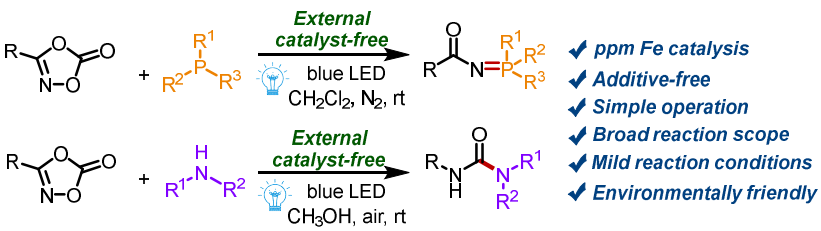
Abstract: A visible-light-induced external catalyst-free decarboxylation of dioxazolones was realized for the bond formation of N=P and N–C bonds to access phosphinimidic amides and ureas. Various phosphinimidic amides and ureas (47 examples) were synthesized with high yields (up to 98%) by this practical strategy in the presence of the system's ppm Fe.

Keywords: dioxazolones; visible light; decarboxylation; phosphinimidic amides; ureas

1. Introduction

Nowadays, the development of clean, environmentally friendly, and efficient chemical processes has become one of the goals of sustainable chemistry [1–4]. Visible light, as a safe, abundant, and renewable natural energy source, has promoted many feasible and valuable transformations [5–8]. Photocatalytic strategies were widely recognized as an attractive "green synthesis pathway" in organic transformations, which are promising from the standpoint of an environmentally friendly and sustainable perspective [9–18]. Despite the simple operation and mild reaction conditions, a precious metal complex or a synthetically elaborate organic dye is usually required [19–22]. It is of great significance to develop cleaner and greener photochemical pathways in the external catalyst-free protocol [23–27].

Nitrene intermediates have attracted great interest from chemists, due to their high reactivity [28–36]. Nitrene-based transformations allow the direct installation of nitrogen-containing building blocks into molecular backbones to build structurally complex compounds [37–40]. In the past few decades, a series of nitrene precursors were reported, such as organic azides [41,42], iminoiodinanes [43,44], amide N-O compounds [45,46], dioxazolones [47–50], and so on. Among them, dioxazolones are highly attractive because of their high activity, stability, convenience, and high coordination ability [51–53]. Herein, we present a visible-light-induced strategy to build N=P and N–C bonds for the generation of phosphinimidic amides and ureas from the reaction of dioxazolones and triarylphosphines or secondary amines (Scheme 1). The transformations are realized without any other catalyst or additive at room temperature. The ppm Fe in the reactants, confirmed by ICP-MS, might play an important role in this reaction.



Scheme 1. The construction of N=P and N–C bonds from dioxazolones.

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Citation: Pan, J.; Li, H.; Sun, K.; Tang, S.; Yu, B. Visible-Light-Induced Decarboxylation of Dioxazolones to Phosphinimidic Amides and Ureas. *Molecules* **2022**, *27*, 3648. https://doi.org/10.3390/molecules27123648

Academic Editors: Daoshan Yang and Zhanhui Yang

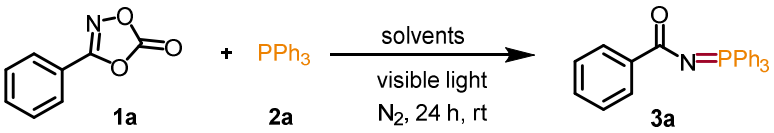
Received: 5 May 2022
Accepted: 4 June 2022
Published: 7 June 2022

2. Results and Discussion

Optimization of the Reaction Conditions

We commenced our study with the model reaction between 3-phenyl-1,4,2-dioxazol-5-one (**1a**) and triphenylphosphine (**2a**) under visible light and N_2 atmosphere. The results are shown in Table 1. Initially, the reaction was carried out by employing DCE as the solvent under irradiation of 10 W 430 nm blue LED at room temperature, and the desired product *N*-(triphenyl-λ^5-phosphinylidene)benzamide (**3a**) could be detected in 11% yield (entry 1). Afterwards, the solvent effect on the yield was investigated (entries 2–8). Different solvents, such as 1,4-dioxane, CH_3OH, acetone, CH_3CN, DMF, THF, and CH_2Cl_2, were surveyed, and the reaction exhibited excellent reaction performance in CH_2Cl_2 to provide the target product in 81% yield (entry 8). Further examination of the wavelengths of LED and substrate ratios showed no more positive results (entries 9–14). Control reactions confirmed that nearly no amidation product **3a** was detected at room temperature in the absence of visible light (entry 15). Moreover, when the reaction was carried out in the air, only a trace amount of the product **3a** was detected (entry 16). Therefore, the optimized reaction conditions were illustrated as follows: **1a** (0.1 mmol); **2a** (0.1 mmol); and CH_2Cl_2 (1 mL) in a N_2 atmosphere under the irradiation of 430 nm blue LED (10 W) for 24 h at room temperature (entry 8).

Table 1. Optimization of reaction conditions [a].

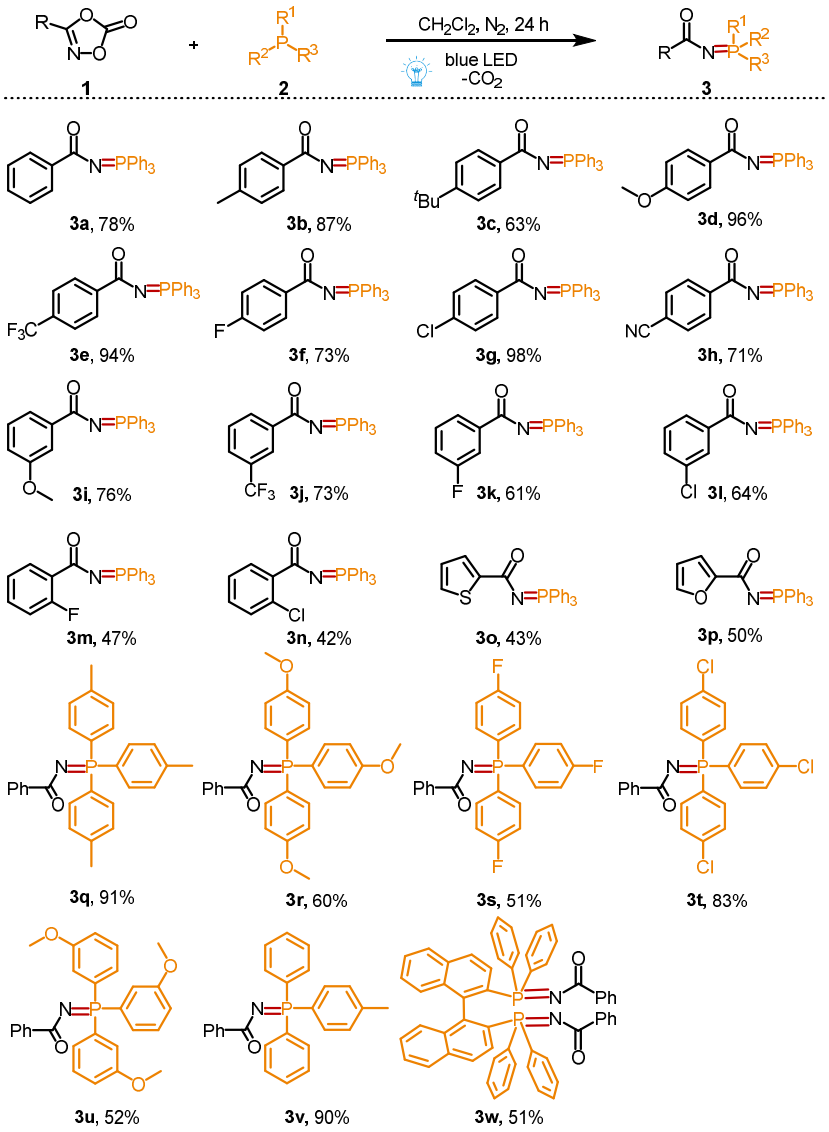


Entry	Solvent	Wavelength	Yield (%)
1	DCE	430 nm	11
2	1,4-dioxane	430 nm	23
3	CH_3OH	430 nm	14
4	Acetone	430 nm	23
5	DMF	430 nm	22
6	CH_3CN	430 nm	26
7	THF	430 nm	0
8	CH_2Cl_2	430 nm	81
9	CH_2Cl_2	460 nm	22
10	CH_2Cl_2	390 nm	63
11 [b]	CH_2Cl_2	Green LED	0
12 [c]	CH_2Cl_2	White LED	0
13 [d]	CH_2Cl_2	430 nm	61
14 [e]	CH_2Cl_2	430 nm	67
15 [f]	CH_2Cl_2	–	0
16 [g]	CH_2Cl_2	430 nm	<5

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol) in solvent (1 mL) at room temperature for 24 h under the irradiation of 10 W 430 nm blue LED. Yield is determined by ^{31}P NMR; [b] Green LED (10 W); [c] White LED (10 W); [d] **1a** (0.2 mmol); [e] **2a** (0.2 mmol); [f] Without light; [g] Reaction in air.

With the optimized conditions in hand, the scope of the organophosphorus compounds and dioxazolones **1** was investigated (Scheme 2). To our delight, various 3-phenyl dioxazolones bearing different electron-donating groups (-CH_3, -^{t}Bu, and -OCH_3) or electron-withdrawing groups (-CF_3, -F, -Cl, and -CN) on the phenyl ring at different positions could react smoothly with **2a** to produce the desired products (**3a**–**3n**) in moderate to excellent yields (42–98%). Among these cases, a slight steric hindrance effect was observed, and para-substituted 3-phenyl dioxazolones (**3a**–**3h**, 63–98%) showed higher reaction reactivities than those of ortho-substituted 3-phenyl dioxazolones (**3m**–**3n**, 42–47%). Moreover, the desired products **3o** and **3p**, which contain the skeletons of thiophene and furan, could also be successfully obtained in 43% and 50% of the yields, respectively. Additionally, electron-poor

and electron-rich triphenylphosphine derivatives were all applicable to this transformation to access the desired products (**3q**–**3v**) in 51–91% yields. In addition, the phosphorus ligand, 1.1′-binaphthyl-2.2′-diphenylphosphine (BINAP), was also a suitable substrate to react with **1a**, providing the corresponding product **3w** in 51% yield.

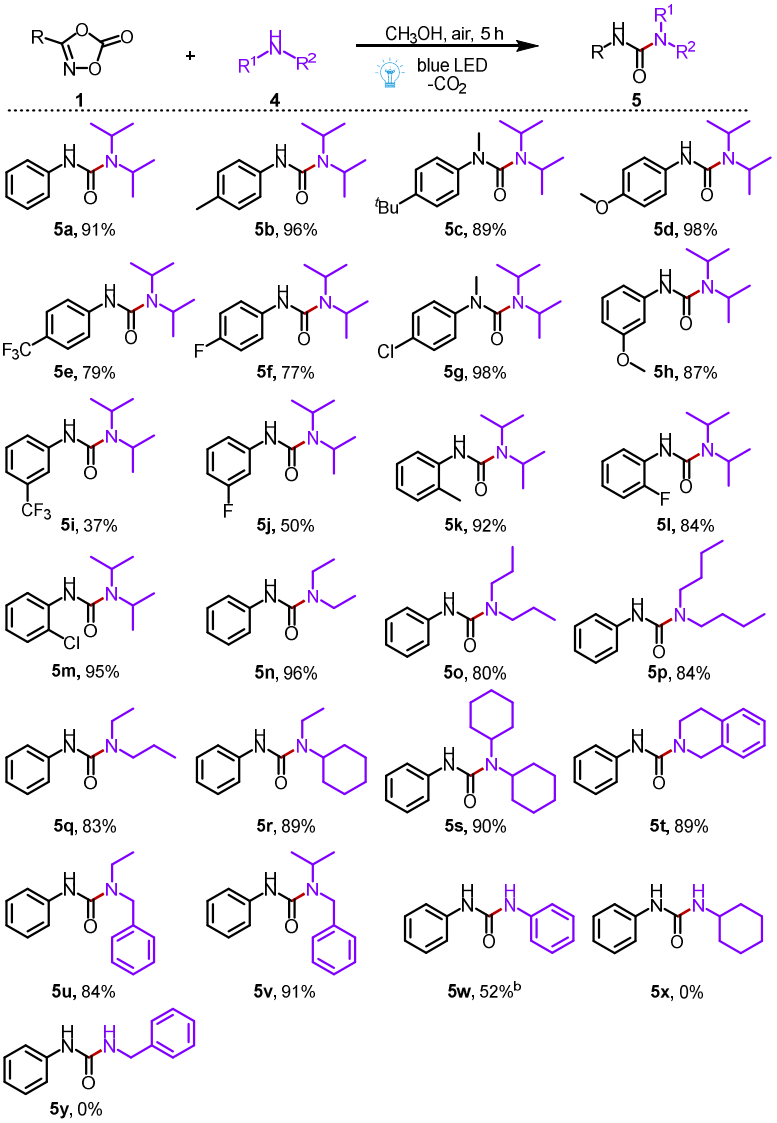


Scheme 2. Substrate scope for the synthesis of phosphinimidic amides.

Reaction conditions: **1a** (0.2 mmol); **2a** (0.2 mmol) in solvent (2 mL) at room temperature for 24 h under the irradiation of 10 W 430 nm blue LED. Isolated yields were given.

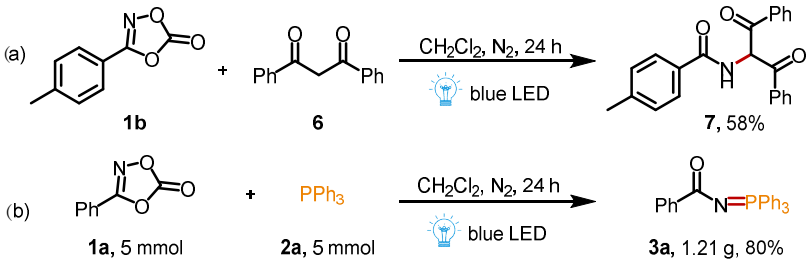
Then, we expanded the photocatalytic decarboxylation reaction of dioxazolones to the synthesis of unsymmetrical urea compounds (Scheme 3). To our delight, a wide range of 3-phenyl dioxazolones all reacted efficiently with diisopropylamine **4a** to furnish the corresponding aryl ureas (**5a**–**5m**) in moderate to excellent yields (37–98%). In these cases, 3-phenyl dioxazolones bearing electron-donating groups (-CH_3, -^{t}Bu, and -OCH_3) showed a better reaction efficiency than those of 3-phenyl dioxazolones bearing electron-withdrawing groups (-CF_3, -F, -Cl). Moreover, the broad scope of the commercially available secondary amines all reacted smoothly in this transformation, adding to the formation of desired ureas (**5n**–**5v**) in good to excellent yields (80–96%). In addition, the primary amine, such as aniline, was also a suitable substrate for reaction with **1a**, providing the corresponding product **5w** in 52% yield. However, cyclohexylamine (**4l**) and benzylamine (**4m**) were not

suitable in this transformation to react with **1a** to access the corresponding products **5x** and **5y**. Compared with the previous report [32], our method effectively avoids the harsh conditions of high temperature, showing good sustainability.



Scheme 3. Substrate scope for the synthesis of ureas. Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol) in solvent (2 mL) at room temperature for 5 h under the irradiation of 10 W 430 nm blue LED. Isolated yields were given; [b] 20 h.

To our satisfaction, this method is also suitable for the reaction between 3-(*p*-tolyl)-1,4,2-dioxazol-5-one **1b** and 1,3-diphenylpropane-1,3-dione **6** to give the corresponding amide product in 58% yield (Scheme 4a), which was previously reported in the presence of additional $FeCl_3$ catalyst [29]. To verify the practicability of this synthetic protocol, the gram-scale synthesis of **3a** was carried out (for details, see the Supplementary Materials). When the reaction was performed at a 5 mmol scale, the desired product **3a** was isolated in 80% yield, indicating that this approach has a good practicability and application prospect (Scheme 4b).



Scheme 4. (**a**) Preparation of amide compounds; (**b**) gram-scale synthesis of **3a**.

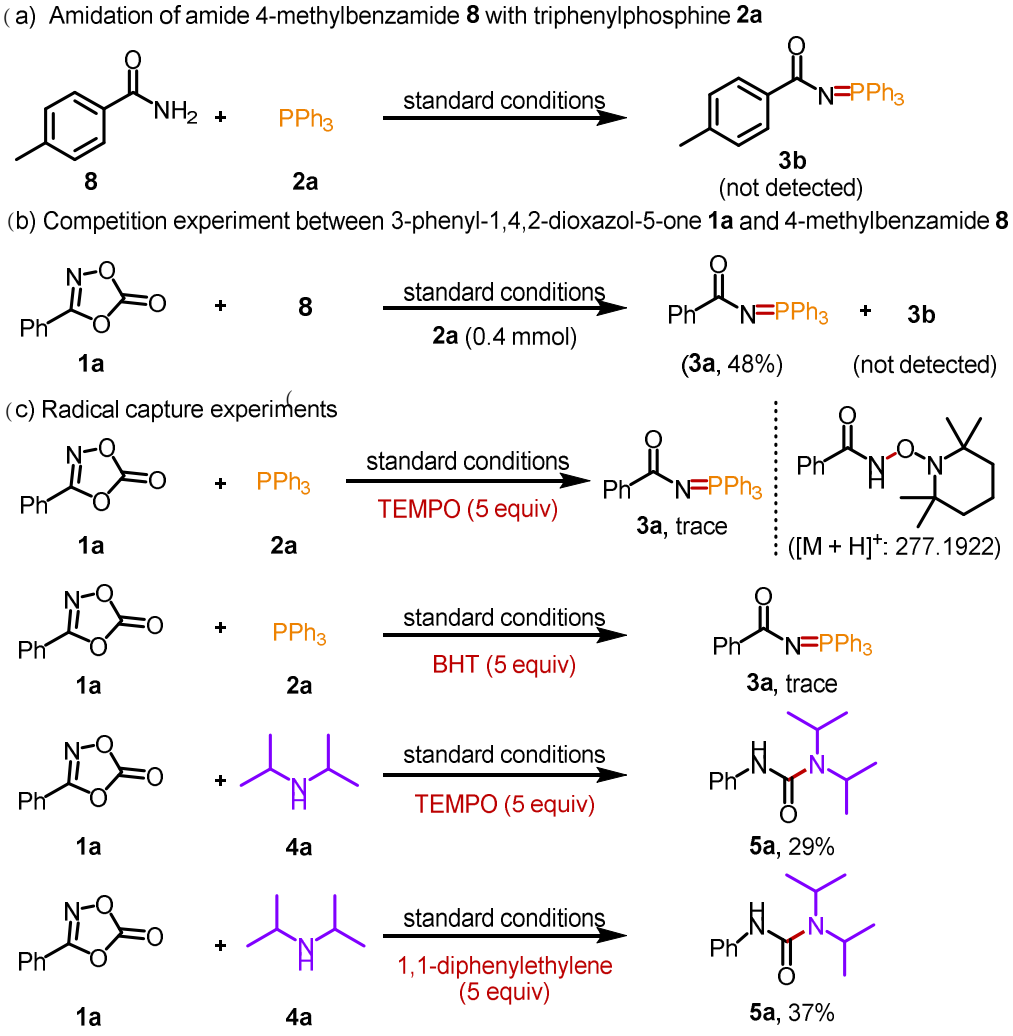
Furthermore, we also evaluated the sensitivity of the reaction of **1a** and **2a**. Compared with the standard conditions, the changes in concentration, temperature, oxygen level, water level, light intensity, and scale were measured. The yields were measured by ^{31}P NMR and the yield deviation was calculated (for details, see the Supplementary Materials). Among them, light intensity and oxygen levels are important parameters for the reaction. Moreover, this transformation is moderately sensitive to water. Other parameters, such as concentration and temperature, can be regarded as random errors, which have a negligible impact on reaction efficiency (Figure S4, Supplementary Materials).

Next, we calculated the E-factor [54,55] and EcoScale scores [56,57] of the chemical process to evaluate the safety, economic, and ecological properties of the method. The results are summarized in Tables S2–S5, Supplementary Materials. As can be seen, the E-factor is extremely low at 0.38 and 0.82, respectively, and the EcoScale penalty is also low, at 21.5 and 15.5. Both parameters reflect the excellent green chemistry metrics of the protocol.

To understand the mechanism of this transformation, a set of control experiments were performed (Scheme 5). The phosphorylation of 4-methylbenzamide **8** with triphenylphosphine **2a** was performed to determine whether the N=P bond was formed through the amide intermediate. However, 4-methyl-*N*-(triphenyl-λ^5-phosphaneylidene) benzamide **3b** was not detected (Scheme 5a). Moreover, intermolecular competition experiments of **1a** and **8** were conducted, and only product **3a** was obtained with 48% yield (Scheme 5b). These results demonstrated that the phosphorylation of dioxazolones was not conducted through amide intermediates. Furthermore, various radical trapping experiments were conducted (Scheme 5c). When (2,2,6,6-tetramethylpiperidine-1-yl)oxidanyl (TEMPO) was added to the model reaction under standard conditions, the reaction was significantly inhibited. The TEMPO-trapped acyl nitrene adducts were detected by high-resolution mass spectrometry (HRMS), with peaks at 277.1922 *m/z*. Subsequently, when another radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol (BHT), was subjected under standard conditions, the reaction was also severely suppressed, indicating a radical process in the phosphorylation of dioxazolone with triphenylphosphine. Then, the radical trapping experiments of **1a** and **4a** were conducted (Scheme 5c). The decreased yields of product **5a** indicated that the transformation also involved a radical process.

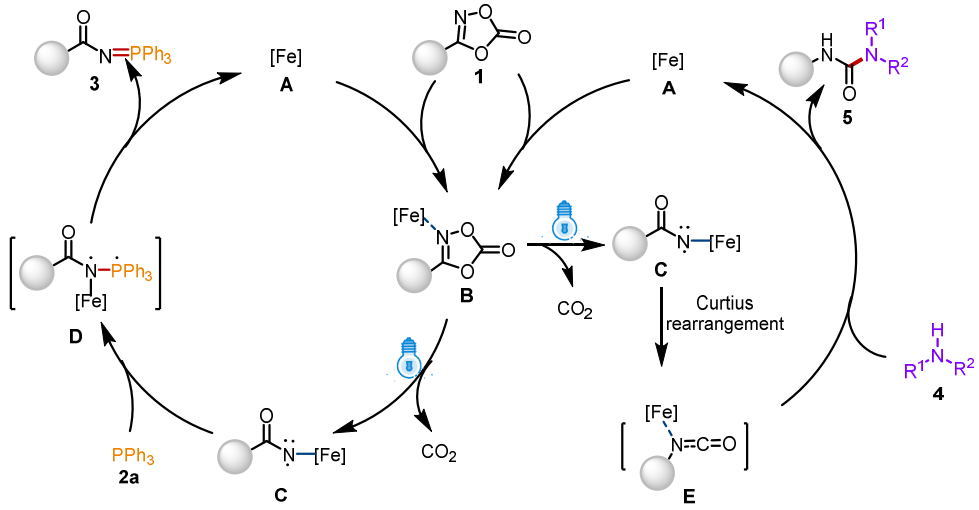
In 2021, Yu and Bao et al., disclosed that $FeCl_3$ (15 mol%) was required for the imidization of phosphines with dioxazolones under visible light irradiation [29]. While in our case, the transformations worked very well without any other additives. Considering the contamination issues in coupling reactions [58], we reasoned that some iron contamination might be possible in the manufacture of the starting materials. Therefore, the model reaction mixture was analyzed with inductively coupled plasma mass spectrometry (ICP-MS). Consequently, it is found that the Fe content of the reactions for the preparation of phosphinimidic amide (**3a**) and urea (**5a**) is approximately 27 ppm and 3 ppm, respectively (for details, see the Supplementary Materials). ICP-MS experiments were also performed on the starting materials of the model reactions (dioxazolone, PPh_3, and amine), and the results showed that the iron contents of the dioxazolone, PPh_3, and amine were 123 ppm, 420 ppm, and 0.9 ppm, respectively (for details, see the Supplementary Materials). It is reasoned that iron contamination issues in commercial chemicals are unavoidable during the production and transportation processes. When additional iron catalyst $FeCl_3$ (5 mol%) was added

to the model reaction under standard conditions, the reaction time was shortened and the yield was increased. These results confirmed that this reaction could be facilitated by iron catalysis (for details, see the Supplementary Materials). These results suggest that, although it is not a real transition-meta-free system, it is still a synthetically useful procedure for the synthesis of phosphinimidic amides and ureas, especially from an industrial chemistry standpoint.



Scheme 5. Control experiments.

Based on these control experiments and previous literature reports, a plausible reaction pathway is proposed in Scheme 6. Initially, the N atom of dioxazolones **1** coordinates with the Fe center to form complex **B**, which is excited by visible light to generate the highly active iron-aminyl radical **C** with the release of CO_2. Subsequently, radical **C** reacts with triphenylphosphine **2a** to form the complex **D**, followed by a reduction and elimination process to obtain product **3**. On the other hand, intermediate **C** underwent Curtius rearrangement to form intermediate **E**, which further reacts with secondary amines **4** to obtain product **5**.



Scheme 6. Proposed reaction mechanism.

3. Experimental Section

3.1. General Information

All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz in $CDCl_3$ at room temperature (20 ± 3 °C), by using tetramethylsilane as the internal standard. High-resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique.

Photochemical reactions were carried out under visible light irradiation by a blue LED at 25 °C. The RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system (Figure S1, Supplementary Materials). Eight 10 W blue LEDs were equipped in this photochemical reactor. The wavelength for blue LED is 430 nm, peak width at half-height is 18.4 nm (Figure S2, Supplementary Materials). The distance from the light source to the irradiation vessel was approximately 15 mm.

*3.2. General Experimental Procedures for the Synthesis of (**3a–3w**)*

In a 25 mL reaction tube, dioxazolones **1** (0.2 mmol, 1.0 equiv), organic phosphine substrate **2** (0.2 mmol, 1.0 equiv) in 1 mL CH_2Cl_2 were allowed to stir with irradiation of 10 W blue LED under N_2 atmosphere at room temperature for 24 h. After the reaction, the solvent was evaporated under vacuum, and the residue was purified by column chromatography on silica gel to afford the desired products **3a**–**3w**.

N-(triphenyl-λ^5-phosphanylidene)benzamide (**3a**):

White solid (59.7 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45–8.38 (m, 2H), 7.94–7.85 (m, 6H), 7.62–7.55 (m, 3H), 7.54–7.41 (m, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3 (d, $J_{C\text{-}P}$ = 8.0 Hz), 138.7 (d, $J_{C\text{-}P}$ = 20.6 Hz), 133.2 (d, $J_{C\text{-}P}$ = 10.0 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.7, 129.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.4 (d, $J_{C\text{-}P}$ = 99.7 Hz), 127.7; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.71;

4-methyl-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3b**):

White solid (69.0 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.2 Hz, 2H), 7.92–7.85 (m, 6H), 7.62–7.55 (m, 3H), 7.53–7.47 (m, 6H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5 (d, $J_{C\text{-}P}$ = 8.1 Hz), 140.9, 135.9 (d, $J_{C\text{-}P}$ = 20.5 Hz), 133.2 (d, $J_{C\text{-}P}$ = 9.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 129.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 99.6 Hz), 128.4, 21.6; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.47;

4-(tert-butyl)-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3c**):

White solid (55.0 mg, 63%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.5 Hz, 2H), 7.92–7.84 (m, 6H), 7.61–7.55 (m, 3H), 7.53–7.45 (m, 8H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4 (d, $J_{C\text{-}P}$ = 8.1 Hz), 153.9, 136.0 (d, $J_{C\text{-}P}$ = 20.5 Hz), 133.2 (d,

J_{C-P} = 10.1 Hz), 132.2 (d, J_{C-P} = 2.9 Hz), 129.4 (d, J_{C-P} = 2.6 Hz), 128.7 (d, J_{C-P} = 12.4 Hz), 128.5 (d, J_{C-P} = 99.3 Hz), 124.6, 34.9, 31.4; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.24;

4-methoxy-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3d**):

White solid (79 mg, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 8.8 Hz, 2H), 7.91–7.84 (m, 6H), 7.60–7.54 (m, 3H), 7.52–7.46 (m, 6H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1 (d, J_{C-P} = 7.8 Hz), 161.8, 133.2 (d, J_{C-P} = 9.9 Hz), 132.2 (d, J_{C-P} = 2.9 Hz), 131.5, 131.4 (d, J_{C-P} = 2.5 Hz), 128.7 (d, J_{C-P} = 12.2 Hz), 128.5 (d, J_{C-P} = 99.6 Hz), 112.8, 55.3; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.30;

4-(trifluoromethyl)-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3e**):

White solid (87.6 mg, 94%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 8.1 Hz, 2H), 7.91–7.84 (m, 6H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.64–7.57 (m, 3H), 7.56–7.49 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8 (d, J_{C-P} = 7.7 Hz), 142.0 (d, J_{C-P} = 21.0 Hz), 133.2 (d, J_{C-P} = 10.3 Hz), 132.5 (d, J_{C-P} = 2.9 Hz), 132.2 (q, J_{C-F} = 32.0 Hz), 129.8 (d, J_{C-P} = 2.5 Hz), 128.8 (d, J_{C-P} = 12.4 Hz), 127.9 (d, J_{C-P} = 99.7 Hz), 124.7 (q, J_{C-F} = 3.8 Hz), 124.3 (q, J_{C-F} = 272.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.40; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −62.47;

4-fluoro-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3f**):

White solid (57.5 mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (dd, *J* = 8.7, 5.9 Hz, 2H), 7.90–7.82 (m, 6H), 7.61–7.56 (m, 3H), 7.55–7.46 (m, 6H), 7.08 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.3 (d, J_{C-P} = 8.0 Hz), 164.7 (d, J_{C-F} = 249.4 Hz), 134.9 (d, J_{C-P} = 20.1 Hz), 133.2 (d, J_{C-P} = 10.1 Hz), 132.3 (d, J_{C-P} = 2.9 Hz), 131.8 (dd, J_{C-F} = 8.9, J_{C-P} = 2.3 Hz), 128.7 (d, J_{C-P} = 12.3 Hz), 128.2 (d, J_{C-P} = 99.7 Hz), 114.4 (d, J_{C-F} = 21.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.87; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −110.66;

4-chloro-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3g**):

White solid (81.8 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.5 Hz, 2H), 7.91–7.82 (m, 6H), 7.62–7.55 (m, 3H), 7.54–7.48 (m, 6H), 7.39 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.2 (d, J_{C-P} = 7.9 Hz), 137.2 (d, J_{C-P} = 21.2 Hz), 136.8, 133.2 (d, J_{C-P} = 9.7 Hz), 132.4 (d, J_{C-P} = 2.9 Hz), 131.1 (d, J_{C-P} = 2.3 Hz), 128.8 (d, J_{C-P} = 12.4 Hz), 128.1 (d, J_{C-P} = 99.7 Hz), 127.8; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.05;

4-cyano-*N*-(triphenyl-λ^5-phosphaneylidene)benzamide (**3h**):

White solid (57.6 mg, 71%), mp 185.5–187.1 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 8.1 Hz, 2H), 7.89–7.80 (m, 6H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.64–7.57 (m, 3H), 7.56–7.49 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.2 (d, J_{C-P} = 8.1 Hz), 142.8 (d, J_{C-P} = 21.3 Hz), 133.1 (d, J_{C-P} = 9.7 Hz), 132.6 (d, J_{C-P} = 3.0 Hz), 131.6, 130.0 (d, J_{C-P} = 2.3 Hz), 128.9 (d, J_{C-P} = 12.4 Hz), 127.7 (d, J_{C-P} = 99.8 Hz), 119.1, 113.8; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.79. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{20}N_2OP$, 407.1308; found, 407.1309;

3-methoxy-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3i**):

White solid (62.4 mg, 76%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.93–7.83 (m, 7H), 7.61–7.55 (m, 3H), 7.54–7.47 (m, 6H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.06–7.01 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1 (d, J_{C-P} = 8.1 Hz), 159.3, 140.2 (d, J_{C-P} = 20.5 Hz), 133.2 (d, J_{C-P} = 9.7 Hz), 132.3 (d, J_{C-P} = 2.9 Hz), 128.7 (d, J_{C-P} = 12.5 Hz), 128.3 (d, J_{C-P} = 99.2 Hz), 122.3 (d, J_{C-P} = 2.6 Hz), 117.4, 113.8 (d, J_{C-P} = 2.9 Hz), 55.4; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.70;

3-(trifluoromethyl)-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3j**):

White solid (65.1 mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 8.57 (d, *J* = 7.7 Hz, 1H), 7.92–7.84 (m, 6H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.64–7.58 (m, 3H), 7.57–7.50 (m, 7H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7 (d, J_{C-P} = 7.7 Hz), 139.5 (d, J_{C-P} = 21.2 Hz), 133.2 (d, J_{C-P} = 10.2 Hz), 132.8, 132.4 (d, J_{C-P} = 3.0 Hz), 130.1 (q, J_{C-F} = 32.2 Hz), 128.8 (d, J_{C-P} = 12.4 Hz), 128.2, 128.0 (d, J_{C-P} = 99.8 Hz), 127.1 (q, J_{C-F} = 3.8 Hz), 126.5 (q, J_{C-F} = 3.5 Hz), 123.0 (q, J_{C-F} = 272.2 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.62; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −62.33;

3-fluoro-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3k**):

White solid (48.7 mg, 61%), mp 154.6–156.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.7 Hz, 1H), 8.10–8.05 (m, 1H), 7.91–7.82 (m, 6H), 7.63–7.56 (m, 3H), 7.55–7.48 (m, 6H), 7.42–7.34 (m, 1H), 7.19–7.13 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.0 (d, J_{C-P} = 7.4 Hz), 162.6 (d, J_{C-F} = 244.8 Hz), 141.2 (d, J_{C-F} = 21.3 Hz), 133.2 (d, J_{C-P} = 10.0 Hz), 132.4 (d, J_{C-F} = 2.9 Hz), 129.1 (d, J_{C-P} = 7.7 Hz), 128.8 (d, J_{C-P} = 12.4 Hz), 128.1 (d, J_{C-P} = 99.8 Hz), 125.1 (d, J_{C-P} = 2.8 Hz), 117.5 (d, J_{C-P} = 21.6 Hz), 116.4 (dd, J_{C-F} = 22.2, J_{C-P} = 2.6 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.13; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −114.38. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{20}FNOP$, 400.1261; found, 400.1261;

3-chloro-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3l**):

Colorless liquid (56.7 mg, 64%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40–8.36 (m, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.90–7.82 (m, 6H), 7.63–7.57 (m, 3H), 7.55–7.48 (m, 6H), 7.46–7.41 (m, 1H), 7.37–7.32 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.9 (d, J_{C-P} = 8.0 Hz), 140.6 (d, J_{C-P} = 21.2 Hz), 133.7, 133.2 (d, J_{C-P} = 10.2 Hz), 132.4 (d, J_{C-P} = 2.6 Hz), 130.6, 129.8 (d, J_{C-P} = 2.7 Hz), 129.0, 128.8 (d, J_{C-P} = 12.0 Hz), 128.0 (d, J_{C-P} = 99.8 Hz), 127.6 (d, J_{C-P} = 2.2 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.40. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{20}ClNOP$, 416.0966; found, 416.0963;

2-fluoro-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3m**):

White solid (37.5 mg, 47%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22–8.16 (m, 1H), 7.93–7.84 (m, 6H), 7.61–7.55 (m, 3H), 7.53–7.47 (m, 6H), 7.41–7.34 (m, 1H), 7.18–7.06 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1 (dd, J_{C-P} = 7.9 Hz, J_{C-F} = 3.6 Hz), 161.9 (d, J_{C-F} = 255.2 Hz), 133.2 (d, J_{C-P} = 10.1 Hz), 132.4 (dd, J_{C-P} = 2.3 Hz, J_{C-F} = 2.2 Hz), 132.3 (d, J_{C-P} = 2.9 Hz), 131.7 (d, J_{C-F} = 8.8 Hz), 128.7 (d, J_{C-P} = 12.4 Hz), 128.0 (d, J_{C-P} = 99.3 Hz), 127.5 (dd, J_{C-P} = 21.4 Hz, J_{C-F} = 9.9 Hz), 123.3 (d, J_{C-F} = 3.8 Hz), 116.5 (d, J_{C-F} = 23.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.39; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −111.60;

2-chloro-*N*-(triphenyl-λ^5-phosphanylidene)benzamide (**3n**):

White solid (35.0 mg, 42%), mp 196.6–197.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43–8.36 (m, 2H), 7.92–7.84 (m, 6H), 7.62–7.56 (m, 3H), 7.54–7.48 (m, 6H), 7.46–7.41 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4 (d, J_{C-P} = 8.6 Hz), 138.6 (d, J_{C-P} = 20.6 Hz), 133.2 (d, J_{C-P} = 9.7 Hz), 132.3 (d, J_{C-P} = 2.9 Hz), 130.7, 129.6 (d, J_{C-P} = 2.3 Hz), 128.7 (d, J_{C-P} = 12.3 Hz), 128.4 (d, J_{C-P} = 99.5 Hz), 127.7; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.72. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{20}ClNOP$, 416.0966; found, 416.0969;

N-(triphenyl-λ^5-phosphanylidene)thiophene-2-carboxamide (**3o**):

Brown solid (33.3 mg, 43%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89–7.82 (m, 6H), 7.80 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.62–7.56 (m, 3H), 7.53–7.47 (m, 6H), 7.40 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.10–7.01 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1 (d, J_{C-P} = 7.0 Hz), 145.2 (d, J_{C-P} = 24.3 Hz), 133.2 (d, J_{C-P} = 9.7 Hz), 132.3 (d, J_{C-P} = 2.9 Hz), 130.2 (d, J_{C-P} = 2.8 Hz), 129.6, 128.7 (d, J_{C-P} = 12.4 Hz), 128.1 (d, J_{C-P} = 99.7 Hz), 127.3; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 19.47;

N-(triphenyl-λ^5-phosphanylidene)furan-2-carboxamide (**3p**):

White solid (37.2 mg, 50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87–7.79 (m, 6H), 7.59–7.53 (m, 3H), 7.51–7.45 (m, 7H), 7.17 (d, *J* = 3.3 Hz, 1H), 6.44 (dd, *J* = 3.2, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0 (d, J_{C-P} = 6.7 Hz), 152.8 (d, J_{C-P} = 26.0 Hz), 144.0, 133.2 (d, J_{C-P} = 10.1 Hz), 132.4, 128.7 (d, J_{C-P} = 12.4 Hz), 127.9 (d, J_{C-P} = 100.2 Hz), 114.3, 111.3; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.86;

N-(tri-*p*-tolyl-λ^5-phosphanylidene)benzamide (**3q**):

White solid (77.1 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 7.8 Hz, 2H), 7.79 (dd, *J* = 12.2, 7.7 Hz, 6H), 7.48–7.41 (m, 3H), 7.32 (dd, *J* = 8.3, 2.8 Hz, 6H), 2.43 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2 (d, J_{C-P} = 8.0 Hz), 142.7 (d, J_{C-P} = 2.9 Hz), 138.9 (d, J_{C-P} = 20.8 Hz), 133.2 (d, J_{C-P} = 10.3 Hz), 130.6, 129.6 (d, J_{C-P} = 2.3 Hz), 129.4 (d, J_{C-P} = 12.9 Hz), 127.6, 125.4 (d, J_{C-P} = 102.0 Hz), 21.7; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.63;

N-(tri-*p*-methoxyphenyl-λ^5-phosphanylidene)benzamide (**3r**):

White solid (56.7 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40–8.34 (m, 2H), 7.78 (dd, *J* = 11.7, 8.8 Hz, 6H), 7.46–7.38 (m, 3H), 7.00 (dd, *J* = 8.9, 2.3 Hz, 6H), 3.85 (s,

9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1 (d, J_{C-P} = 7.4 Hz), 162.6 (d, J_{C-P} = 2.9 Hz), 139.0 (d, J_{C-P} = 20.4 Hz), 135.0 (d, J_{C-P} = 11.1 Hz), 130.5, 129.5 (d, J_{C-P} = 2.3 Hz), 127.6, 119.9 (d, J_{C-P} = 106.5 Hz), 114.3 (d, J_{C-P} = 13.3 Hz), 55.4; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 19.68;

N-(tris(4-fluorophenyl)-λ^5-phosphanylidene)benzamide (**3s**):

White solid (44.2 mg, 51%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34–8.29 (m, 2H), 7.90–7.81 (m, 6H), 7.50–7.41 (m, 3H), 7.26–7.19 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5 (d, J_{C-P} = 8.1 Hz), 165.4 (dd, J_{C-F} = 255.1 Hz, J_{C-P} = 3.2 Hz), 138.1 (d, J_{C-P} = 20.6 Hz), 135.6 (dd, J_{C-F} = 11.7 Hz, J_{C-P} = 8.8 Hz), 131.0, 129.5 (d, J_{C-P} = 2.7 Hz), 127.8, 123.9 (dd, J_{C-P} = 103.9 Hz, J_{C-F} = 3.3 Hz), 116.4 (dd, J_{C-F} = 21.6 Hz, J_{C-P} = 13.6 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 18.98; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −105.30;

N-(tris(4-chlorophenyl)-λ^5-phosphanylidene)benzamide (**3t**):

White solid (80.5 mg, 83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36–8.30 (m, 2H), 7.79 (dd, *J* = 12.0, 8.4 Hz, 6H), 7.54–7.47 (m, 7H), 7.43 (dd, *J* = 8.1, 6.2 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.7 (d, J_{C-P} = 8.0 Hz), 139.5 (d, J_{C-P} = 3.6 Hz), 137.9 (d, J_{C-P} = 20.5 Hz), 134.4 (d, J_{C-P} = 11.0 Hz), 131.1, 129.5 (d, J_{C-P} = 2.5 Hz), 129.4 (d, J_{C-P} = 12.8 Hz), 127.8, 126.2 (d, J_{C-P} = 102.0 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 19.49;

N-(tris(3-methoxyphenyl)-λ^5-phosphaneylidene)benzamide (**3u**):

White solid (48.5 mg, 52%), mp 146.3–147.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41–8.36 (m, 2H), 7.52–7.47 (m, 3H), 7.46–7.34 (m, 9H), 7.12–7.07 (m, 3H), 3.79 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2 (d, J_{C-P} = 7.9 Hz), 159.6 (d, J_{C-P} = 15.4 Hz), 138.7 (d, J_{C-P} = 20.6 Hz), 130.7, 129.9 (d, J_{C-P} = 14.6 Hz), 129.6 (d, J_{C-P} = 99.1 Hz), 129.5 (d, J_{C-P} = 2.4 Hz), 127.7, 125.4 (d, J_{C-P} = 9.7 Hz), 118.4 (d, J_{C-P} = 11.0 Hz), 118.1 (d, J_{C-P} = 2.9 Hz), 55.4; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.38. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{27}NO_4P$, 472.1672; found, 472.1677;

N-(diphenyl(*p*-tolyl)-λ^5-phosphanylidene)benzamide (**3v**):

White solid (71.1 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45–8.37 (m, 2H), 7.93–7.85 (m, 4H), 7.81–7.74 (m, 2H), 7.61–7.55 (m, 2H), 7.53–7.42 (m, 7H), 7.32 (dd, *J* = 8.3, 2.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3 (d, J_{C-P} = 8.0 Hz), 142.9 (d, J_{C-P} = 2.9 Hz), 138.7 (d, J_{C-P} = 20.6 Hz), 133.3 (d, J_{C-P} = 10.5 Hz), 133.2 (d, J_{C-P} = 9.5 Hz), 132.2 (d, J_{C-P} = 3.0 Hz), 130.7, 129.6, 129.5 (d, J_{C-P} = 10.0 Hz), 128.7 (d, J_{C-P} = 12.3 Hz), 128.6 (d, J_{C-P} = 99.8 Hz), 127.7, 124.8 (d, J_{C-P} = 101.3 Hz), 21.7; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.67;

N,*N*′-([1,1′-binaphthalene]-2,2′-diylbis(diphenyl-λ^5-phosphaneylylidene))dibenzamide (**3w**):

White solid (87.7 mg, 51%), mp 184.5–185.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 7.1 Hz, 4H), 7.78–7.69 (m, 6H), 7.57–7.46 (m, 7H), 7.44–7.29 (m, 13H), 7.28–7.21 (m, 3H), 7.20–7.07 (m, 7H), 6.41 (dd, *J* = 8.3, 5.0 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9 (d, J_{C-P} = 8.0 Hz), 159.6 (d, J_{C-P} = 2.0 Hz), 138.8 (d, J_{C-P} = 21.2 Hz), 135.1 (d, J_{C-P} = 7.1 Hz), 134.1 (d, J_{C-P} = 2.6 Hz), 133.3 (d, J_{C-P} = 10.5 Hz), 132.9 (d, J_{C-P} = 10.3 Hz), 132.1 (d, J_{C-P} = 3.0 Hz), 131.6 (d, J_{C-P} = 2.4 Hz), 130.4, 129.4 (d, J_{C-P} = 2.7 Hz), 128.5 (d, J_{C-P} = 12.5 Hz), 128.2 (d, J_{C-P} = 12.6 Hz), 127.8 (d, J_{C-P} = 104.7 Hz), 127.50, 127.45, 123.9 (d, J_{C-P} = 11.4 Hz), 121.0 (d, J_{C-P} = 6.8 Hz), 119.2 (d, J_{C-P} = 100.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 19.95. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{58}H_{43}N_2O_2P_2$, 861.2794; found, 861.2791.

*3.3. General Experimental Procedures for the Synthesis of (***5a**–**5w***)*

In a 25 mL reaction tube, dioxazolone **1** (0.2 mmol, 1.0 equiv.), and amine **4** (0.4 mmol, 2.0 equiv.) in 1 mL CH_3OH were allowed to stir with irradiation of 10 W blue LED at room temperature for 5 h. After the reaction, the solvent was evaporated under vacuum, and the residue was purified by column chromatography on silica gel to afford the desired products **5a**–**5w**.

1,1-diisopropyl-3-phenylurea (**5a**):

White solid (40.1 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.31–7.26 (m, 2H), 7.06–6.99 (m, 1H), 6.26 (s, 1H), 4.04–3.95 (m, 2H), 1.34 (d,

J = 7.0 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 139.4, 128.8, 122.6, 119.7, 45.5, 21.5;

1,1-diisopropyl-3-(*p*-tolyl)urea (**5b**):

White solid (44.9 mg, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.18 (s, 1H), 4.04–3.94 (m, 2H), 2.30 (s, 3H), 1.33 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 136.8, 132.1, 129.3, 119.9, 45.4, 21.5, 20.7;

3-(4-(*tert*-butyl)phenyl)-1,1-diisopropylurea (**5c**):

White solid (49.1 mg, 89%), mp 115.1–116.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33–7.29 (m, 4H), 6.17 (s, 1H), 4.05–3.96 (m, 2H), 1.34 (d, *J* = 6.9 Hz, 12H); 1.31 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 145.6, 136.7, 125.7, 119.7, 45.4, 34.2, 31.4, 21.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{29}N_2O$, 277.2274; found, 277.2284;

1,1-diisopropyl-3-(4-methoxyphenyl)urea (**5d**):

White solid (49.0 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.13 (s, 1H), 4.01–3.92 (m, 2H), 3.77 (s, 3H), 1.32 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 155.1, 132.5, 122.0, 114.1, 55.5, 45.4, 21.5;

1,1-diisopropyl-3-(4-(trifluoromethyl)phenyl)urea (**5e**):

White solid (44.2 mg, 79%), mp 151.9–153.1 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57–7.46 (m, 4H), 6.43 (s, 1H), 4.07–3.92 (m, 2H), 1.35 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.0, 142.6, 126.1 (q, J_{C-F} = 3.8 Hz), 124.4 (q, J_{C-F} = 271.1 Hz), 124.2 (q, J_{C-F} = 32.7 Hz), 118.9, 45.7, 21.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −61.81; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{20}F_3N_2O$, 289.1522; found, 289.1534;

3-(4-fluorophenyl)-1,1-diisopropylurea (**5f**):

White solid (36.7 mg, 77%), mp 134.5–135.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.27 (m, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.31 (s, 1H), 4.03–3.86 (m, 2H), 1.30 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6 (d, J_{C-F} = 241.2 Hz), 154.8, 135.4 (d, emphJ_{C-F} = 2.9 Hz), 121.8 (d, J_{C-F} = 7.9 Hz), 115.2 (d, J_{C-F} = 22.1 Hz), 45.6, 21.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.90; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{20}FN_2O$, 239.1554; found, 239.1567;

3-(4-chlorophenyl)-1,1-diisopropylurea (**5g**):

White solid (49.8 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.29 (s, 1H), 4.03–3.90 (m, 2H), 1.32 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.4, 138.0, 128.7, 127.4, 121.0, 45.6, 21.5;

1,1-diisopropyl-3-(3-methoxyphenyl)urea (**5h**):

White solid (43.6 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20–7.14 (m, 2H), 6.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.57 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.27 (s, 1H), 4.05–3.95 (m, 2H), 3.81 (s, 3H), 1.33 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 154.5, 140.7, 129.4, 111.7, 108.6, 105.1, 55.3, 45.4, 21.5;

1,1-diisopropyl-3-(3-(trifluoromethyl)phenyl)urea (**5i**):

White solid (21.3 mg, 37%), mp 151.2–152.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.62–7.55 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.29–7.25 (m, 1H), 6.37 (s, 1H), 4.07–3.94 (m, 2H), 1.36 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.2, 139.9, 131.2 (q, J_{C-F} = 271.6 Hz), 129.3, 122.7, 119.1 (q, J_{C-F} = 3.7 Hz), 116.1 (q, J_{C-F} = 4.0 Hz), 45.7, 21.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.64. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{20}F_3N_2O$, 289.1522; found, 289.1536;

3-(3-fluorophenyl)-1,1-diisopropylurea (**5j**):

White solid (23.9 mg, 50%), mp 118.5–119.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40–7.32 (m, 1H), 7.23–7.14 (m, 1H), 7.00 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.72–6.64 (m, 1H), 6.39 (s, 1H), 4.03–3.89 (m, 2H), 1.32 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2 (d, J_{C-F} = 243.5 Hz), 154.2, 141.1 (d, J_{C-F} = 11.2 Hz), 129.7 (d, J_{C-F} = 9.6 Hz), 114.7 (d, J_{C-F} = 2.9 Hz), 109.0 (d, J_{C-F} = 21.3 Hz), 106.9 (d, J_{C-F} = 26.4 Hz), 45.6, 21.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.35. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{20}FN_2O$, 239.1554; found, 239.1564;

1,1-diisopropyl-3-(*o*-tolyl)urea (**5k**):

White solid (43.0 mg, 92%), mp 136.8–138.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.23–7.14 (m, 2H), 7.04–6.96 (m, 1H), 6.07 (s, 1H), 4.11–3.99 (m, 2H), 2.28 (s, 3H), 1.36 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 137.6, 130.3, 127.6, 126.7, 123.2, 122.3, 45.4, 21.5, 18.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{23}N_2O$, 235.1805; found, 235.1816;

3-(2-fluorophenyl)-1,1-diisopropylurea (**5l**):

White solid (40.0 mg, 84%), mp 109.1–110.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24–8.16 (m, 1H), 7.13–7.02 (m, 2H), 6.99–6.90 (m, 1H), 6.58 (s, 1H), 4.12–4.03 (m, 2H), 1.35 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.1, 152.3 (d, J_{C-F} = 239.8 Hz), 128.0 (d, J_{C-F} = 9.5 Hz), 124.5 (d, J_{C-F} = 3.6 Hz), 122.0 (d, J_{C-F} = 7.5 Hz), 121.1, 114.3 (d, J_{C-F} = 19.2 Hz), 45.3, 21.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -133.39. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{20}FN_2O$, 239.1554; found, 239.1564;

3-(2-chlorophenyl)-1,1-diisopropylurea (**5m**):

White solid (49.6 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41–7.37 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.06–6.98 (m, 1H), 6.27 (s, 1H), 4.05–3.95 (m, 2H), 1.34 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 139.4, 128.8, 122.6, 119.7, 45.5, 21.5;

1,1-diethyl-3-phenylurea (**5n**):

White solid (36.8 mg, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43–7.39 (m, 2H), 7.31–7.25 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.40 (s, 1H), 3.41–3.35 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.7, 139.4, 128.8, 122.8, 119.9, 41.6, 13.9;

3-phenyl-1,1-dipropylurea (**5o**):

White solid (35 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43–7.37 (m, 2H), 7.31–7.25 (m, 2H), 7.06–6.97 (m, 1H), 6.41 (s, 1H), 3.31–3.24 (m, 4H), 1.71–1.61 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 139.4, 128.8, 122.7, 119.8, 49.4, 21.9, 11.4;

1,1-dibutyl-3-phenylurea (**5p**):

White solid (41.6 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44–7.38 (m, 2H), 7.30–7.25 (m, 2H), 7.05–6.99 (m, 1H), 6.38 (s, 1H), 3.34–3.28 (m, 4H), 1.65–1.58 (m, 4H), 1.43–1.34 (m, 4H), 0.98 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 139.4, 128.8, 122.7, 119.7, 47.5, 30.8, 20.2, 13.9;

1-ethyl-3-phenyl-1-propylurea (**5q**):

Colorless liquid (34.0 mg, 83%), mp 56.3–57.6 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43–7.37 (m, 2H), 7.31–7.25 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.39 (s, 1H), 3.42–3.34 (m, 2H), 3.30–3.24 (m, 2H), 1.71–1.61 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 139.4, 128.8, 122.7, 119.8, 48.8, 42.1, 22.0, 13.8, 11.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{19}N_2O$, 207.1492; found, 207.1499;

1-cyclohexyl-1-ethyl-3-phenylurea (**5r**):

White solid (44.0 mg, 89%), mp 123.5–124.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44–7.39 (m, 2H), 7.31–7.25 (m, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.41 (s, 1H), 4.14–4.03 (m, 1H), 3.33–3.25 (m, 2H), 1.85–1.76 (m, 4H), 1.72–1.64 (m, 1H), 1.47–1.33 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.18–1.06 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 139.5, 128.8, 122.7, 119.9, 54.8, 36.9, 31.5, 26.0, 25.6, 16.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{23}N_2O$, 247.1805; found, 247.1815;

1,1-dicyclohexyl-3-phenylurea (**5s**):

White solid (54.0 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40–7.36 (m, 2H), 7.31–7.25 (m, 2H), 7.04–6.98 (m, 1H), 6.32 (s, 1H), 3.55–3.45 (m, 2H), 1.89–1.81 (m, 6H), 1.80–1.75 (m, 6H), 1.69 (d, *J* = 13.0 Hz, 2H), 1.42–1.31 (m, 4H), 1.22–1.11 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 139.4, 128.8, 122.5, 119.7, 55.5, 31.9, 26.4, 25.6;

N-phenyl-3,4-dihydroisoquinoline-2(1H)-carboxamide (**5t**):

White solid (45.1 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46–7.42 (m, 2H), 7.32–7.27 (m, 2H), 7.25–7.17 (m, 3H), 7.15–7.10 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.75 (s, 1H), 4.67 (s, 2H), 3.72 (t, *J* = 5.9 Hz, 2H), 2.91 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.2, 139.2, 135.0, 133.3, 128.9, 128.4, 126.8, 126.5, 126.4, 123.1, 120.3, 45.8, 41.6, 29.0;

1-benzyl-1-ethyl-3-phenylurea (**5u**):

Colorless liquid (42.8 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42–7.38 (m, 2H), 7.37–7.30 (m, 5H), 7.29–7.24 (m, 2H), 7.06–7.00 (m, 1H), 6.40 (s, 1H), 4.59 (s, 2H), 3.52–3.45 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.4, 139.2, 137.7, 129.0, 128.8, 127.7, 127.1, 122.9, 119.9, 50.3, 42.5, 13.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{19}N_2O$, 255.1492; found, 255.1500;

1-benzyl-1-isopropyl-3-phenylurea (**5v**):

White solid (48.8 mg, 91%), mp 108.8–109.9 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45–7.37 (m, 4H), 7.37–7.32 (m, 1H), 7.25–7.19 (m, 4H), 7.02–6.96 (m, 1H), 6.36 (s, 1H), 4.86–4.73 (m, 1H), 4.47 (s, 2H), 1.24 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.8, 139.3, 138.2, 129.2, 128.7, 127.8, 126.4, 122.8, 119.8, 46.4, 45.5, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{21}N_2O$, 269.1648; found, 269.1657;

1,3-diphenylurea (**5w**):

White solid (22.5 mg, 52%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.7 (s, 2H), 7.5 (dd, *J* = 8.6, 1.2 Hz, 4H), 7.3–7.2 (m, 4H), 7.0–6.9 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.0, 140.2, 129.2, 122.3, 118.6.

4. Conclusions

In conclusion, we have disclosed a visible-light-promoted external catalyst-free procedure for the decarboxylation of dioxazolones to synthesize various phosphinimidic amides and ureas. The method has the advantages of no additional transition metals, economic raw materials, mild reaction conditions, and easy operation. It could be reasoned that the ppm Fe in the reaction mixture played a significant role in this transformation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27123648/s1. References [29,32,34,59–63] are cited in the Supplementary Materials. Synthetic procedure of starting materials, procedure and spectral data of products, copies of ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, ^{19}F-NMR spectra.

Author Contributions: Conceptualization, J.P., H.L. and K.S.; data curation, J.P., H.L. and B.Y.; methodology, J.P. and H.L.; supervision, K.S. and B.Y.; validation, B.Y.; writing—original draft, J.P.; writing—review and editing, K.S. and S.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Hunan Provincial Natural Science Foundation of China (2021JJ40432), and the National Natural Science Foundation of China (21971224, 22171249).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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

Sample Availability: Not available.

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