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Substituent-Controllable Cascade Regioselective Annulation of β-Enaminones with *N*-Sulfonyl Triazoles for Modular Access to Imidazoles and Pyrroles

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Abstract: A controllable synthesis of trisubstituted imidazoles and pyrroles has been developed through rhodium(II)-catalyzed regioselective annulation of *N*-sulfonyl-1,2,3-trizaoles with β-enaminones. The imidazole ring was formed through a 1,1-insertion of the N-H bond to α-imino rhodium carbene, followed by a subsequent intramolecular 1,4-conjugate addition. This occurred when the α-carbon atom of the amino group was bearing a methyl group. Additionally, the pyrrole ring was constructed by utilizing a phenyl substituent and undergoing intramolecular nucleophilic addition. The mild conditions, good tolerance towards functional groups, gram-scale synthesis capability, and ability to undergo valuable transformations of the products qualify this unique protocol as an efficient tool for the synthesis of *N*-heterocycles.

Keywords: annulation; β-enaminones; imidazoles; pyrroles; *N*-sulfonyl trizaoles

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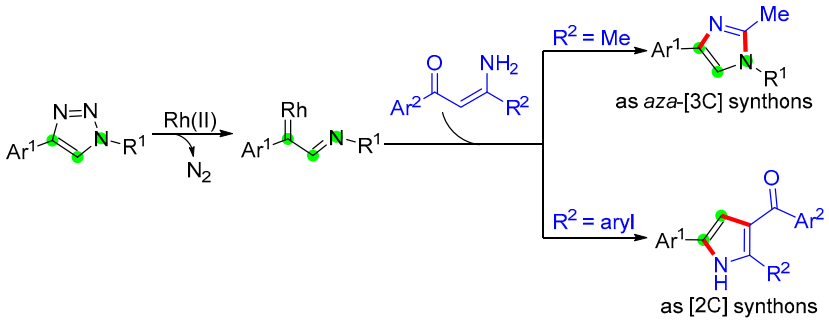
1. Introduction

Nitrogen-containing heterocycles are privileged structural motifs in various natural products and bioactive compounds [1,2]. Among them, imidazole and pyrrole frameworks are very common structural units widely distributed in natural products, pharmaceutics, agrochemicals, and other functional materials [3,4]. For this reason, the synthesis of such compounds continues to be a hot topic in modern synthetic chemistry [5–8]. Consequently, a large number of new reactions have been developed to construct structurally diverse imidazole and pyrrole derivatives, such as multicomponent reactions [9,10]. [3 + 2] cycloaddition [11–14], as well as both metal-catalyzed intermolecular [15,16] and intramolecular [17,18] cyclization strategies. Despite all the achievements, the development of efficient methods for their synthesis, particularly regiocontrolled synthesis of those containing multiple substituents from readily accessible compounds, is of ever-increasing importance.

In the past decades, 1,2,3-triazoles have emerged as capable precursors for the synthesis of various nitrogen heterocycles [19,20]. Upon treatment with rhodium(II) catalysts, *N*-sulfonyl-1,2,3-triazoles readily undergo denitrogenation reactions to form α-imino rhodium carbenes, a versatile intermediate that could promote a wide range of transformations [21,22]. In addition to common reactivities such as cyclopropanation [23,24], X-H insertion [25–28], and ylide formation [29–31], α-imino rhodium carbenes can also serve as [1C]- or aza-[3C]-synthons in stepwise cycloadditions, leading to the formation of various N-heterocycles [32–35]. As a major part of our research efforts in developing new methodologies for the construction of heterocycles [36–39], we herein describe an efficient strategy for the regioselective synthesis of trisubstituted imidazoles and pyrroles. This strategy involves the cascade N-H insertion to α-imino rhodium carbene, followed by

substituent-controllable intramolecular annulation (Scheme 1). In this scheme, the α-imino rhodium carbene acted as [2C] and aza-[3C]-synthons, respectively.



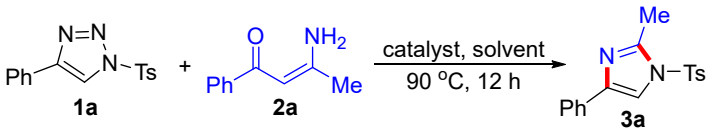
Scheme 1. Substituent-controllable cascade strategy for the synthesis of trisubstituted imidazoles and pyrroles.

2. Results and Discussion

The optimization of a one-pot procedure for the formation of imidazole 3a from triazole **1a** and β-enaminone **2a** was undertaken (Table 1). Screening of various transition-metal catalysts revealed that dirhodium catalysts $Rh_2(OAc)_4$ and $Rh_2(oct)_4$ were demonstrated to be more efficient than other metal catalysts for this reaction (Table 1, entries 1–6). Further investigation showed that a lower catalytic loading (2 mol%) had a positive effect on the reaction (Table 1, entries 7–10). Other solvents, including toluene and chlorobenzene, could better promote this transformation and then utilize chlorobenzene for further optimization (Table 1, entries 11–16). A further variation of reaction temperatures revealed that 80 °C was the optimal condition (Table 1, entries 17–19). The reaction time extension did not benefit the product yield (Table 1, entries 20–22). Thus, the optimal reaction conditions were $Rh_2(oct)_4$ in chlorobenzene at 90 °C for 12 h (Table 1, entry 13).

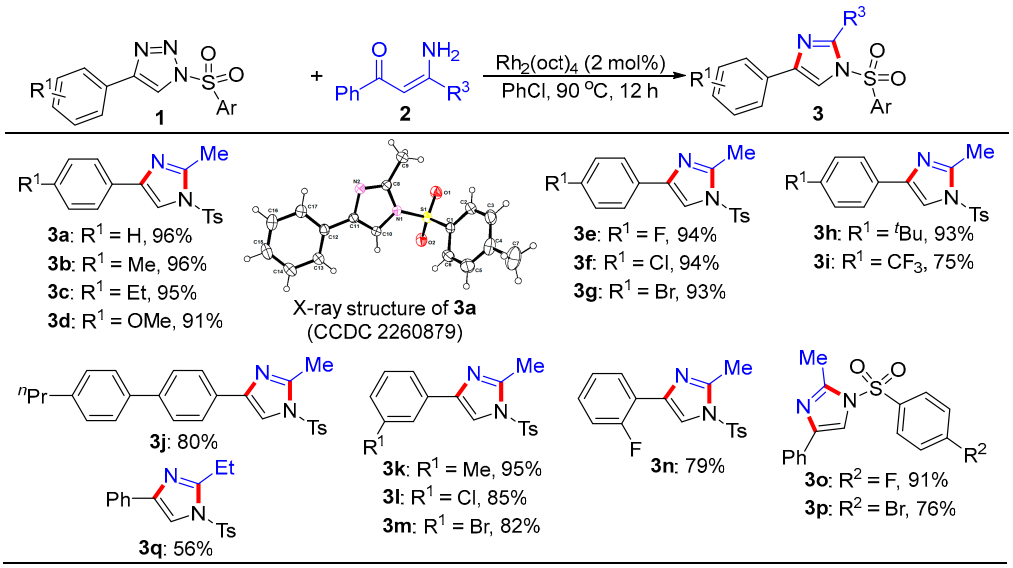
With the optimal conditions in hand, we explored the scope and generality of this [3 + 2] annulation with a combination of various substituted *N*-sulfonyl-1,2,3-triazoles **1** and β-enamino ketones **2** (Scheme 2). We first evaluated the effect of substituents in the R^1 group on the phenyl of *N*-sulfonyl-1,2,3-triazoles. The results indicated that the introduction of electron-neutral (-Me, -Et), electron-rich (-OMe), and electron-deficient (-F, -Cl, -Br) substituents at the *para*-positions was tolerated in this transformation. The desired imidazoles (products **3b**–**3g**) were obtained in yields ranging from 91% to 96%. Notably, the presence of bulky *tert*-butyl or strong electron-withdrawing trifluoromethyl groups at the para-position of benzene ring triazoles **1** led to a smooth reaction process. This resulted in the formation of the corresponding products **3h** and **3i**, with yields of 93% and 75%, respectively. Moreover, the extended π structure did not show an influence, and the desired product **3j** was successfully obtained with an 80% yield. Additionally, substituent variations on the *meta*- and *ortho*-positions could work well to produce the corresponding products **3k**–**3n** in 79–95% yields. Furthermore, the *N*-arylsulfonyl groups of the triazole substrates were also examined. The reactions of fluoro- and bromo-substituted phenylsulfonyl triazoles proceeded well, giving the desired products **3o** and **3p** in 91% and 76% yields, respectively. In addition, (*Z*)-3-amino-1-phenylpent-2-en-1-one was also a viable substrate for the transformation, generating the product **3q** in 56% yield.

Table 1. Optimization of the reaction conditions [a].



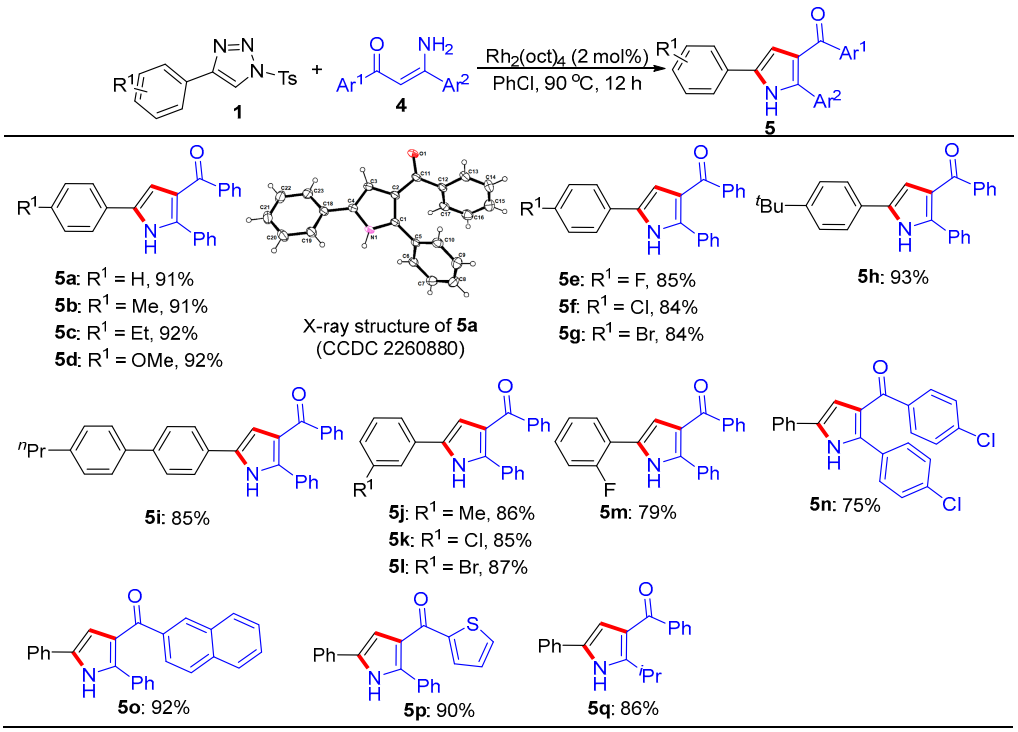
Entry	Catalyst (x mol%)	Solvent	Yield (%) [b]
1	$Rh_2(OAc)_4$ (4)	DCM	56
2	$Rh_2(oct)_4$ (4)	DCM	58
3	CuI (4)	DCM	44
4	$Sc(OTf)_3$ (4)	DCM	trace
5	$Co_2(CO)_8$ (4)	DCM	nr
6	$Ni(acac)_2$ (4)	DCM	nr
7	$Rh_2(oct)_4$ (3)	DCM	73
8	$Rh_2(oct)_4$ (2)	DCM	79
9	$Rh_2(oct)_4$ (1)	DCM	41
10	/	DCM	nr
11	$Rh_2(oct)_4$ (2)	DCE	55
12	$Rh_2(oct)_4$ (2)	toluene	84
13	$Rh_2(oct)_4$ (2)	PhCl	96
14	$Rh_2(oct)_4$ (2)	CH_3OH	trace
15	$Rh_2(oct)_4$ (2)	CH_3NO_2	trace
16	$Rh_2(oct)_4$ (2)	DMF	nr
17 [c]	$Rh_2(oct)_4$ (2)	PhCl	nr
18 [d]	$Rh_2(oct)_4$ (2)	PhCl	87
19 [e]	$Rh_2(oct)_4$ (2)	PhCl	94
20 [f]	$Rh_2(oct)_4$ (2)	PhCl	56
21 [g]	$Rh_2(oct)_4$ (2)	PhCl	78
22 [h]	$Rh_2(oct)_4$ (2)	PhCl	96

[a] Reaction conditions: 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **1a** (0.2 mmol), 3-amino-1-phenylbut-2-en-1-one **2a** (0.2 mmol), and catalyst in solvent (2 mL) at 90 °C for 12 h under an argon atmosphere. [b] Isolated yields. [c] At 60 °C. [d] At 80 °C. [e] At 100 °C. [f] For 2 h. [g] For 6 h. [h] For 18 h. nr = no reaction.



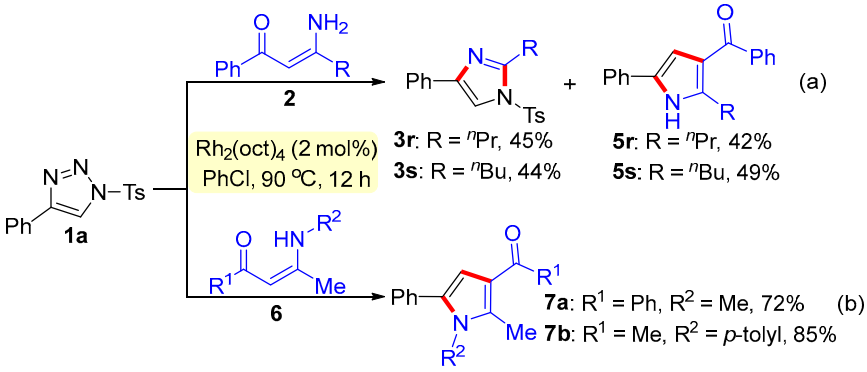
Scheme 2. Substrate scope of *N*-sulfonyl-1,2,3-triazoles and *β*-enaminones for the synthesis of trisubstituted imidazoles. Reaction conditions: *N*-sulfonyl-1,2,3-triazoles **1** (0.2 mmol), *β*-enaminones **2** (0.2 mmol), and $Rh_2(oct)_4$ (2 mol%) in PhCl (2 mL) at 90 °C for 12 h under an argon atmosphere. Isolated yields were reported.

Subsequently, an unexpected pyrrole product **5a** was obtained in 91% yield under standard conditions when the phenyl group (**4a**) replaced the methyl group of *β*-enaminones. We further evaluated the feasibility by using the 1,3-diaryl *β*-enaminones as starting materials (Scheme 3). As expected, a wide range of electronically different substituents, including alkyl, methoxy, halogen, and bulky *tert*-butyl groups, were successfully installed into the products **5a**–**5h**. Moreover, an extended π-system was implemented on the pyrrole structure (product **5i**). Particularly noteworthy is that the halogen groups (e.g., -F, -Cl, and -Br) remained intact during the course of the reaction, which makes this transformation particularly attractive in terms of increasing the molecular complexity via transition metal-catalyzed coupling reactions (**5e**–**5g** and **5k**–**5m**). Additionally, we turned our attention to investigating the suitability of the substrate 1,3-diaryl *β*-enaminones **4**, and the desired products **5n**–**5q** were successfully obtained in 76–92% yields. It was gratifying that the introduction of a naphthyl and thienyl group also proceeded smoothly to produce the desired products **5o** and **5p** in yields of 92% and 90%, respectively. Likewise, changing the phenyl group to a bulky isopropyl was also tolerated in the reaction to give the desired product **5q** in an 86% yield.



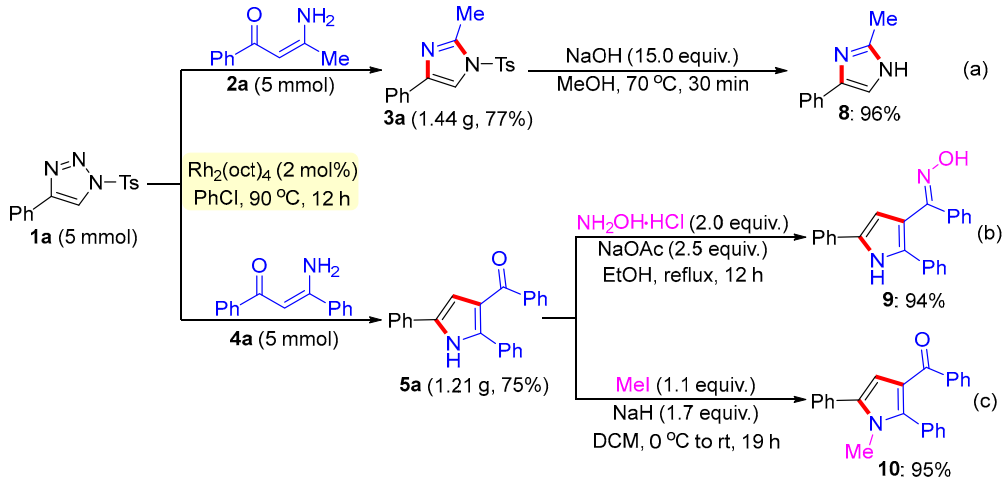
Scheme 3. Substrate scope of *N*-sulfonyl-1,2,3-triazoles and *β*-enaminones for the synthesis of trisubstituted pyrroles. Reaction conditions: *N*-sulfonyl-1,2,3-triazoles **1** (0.2 mmol), *β*-enaminones **2** (0.2 mmol), and $Rh_2(oct)_4$ (2 mol%) in PhCl (2 mL) at 90 °C for 12 h under an argon atmosphere. Isolated yields were reported.

Based on the above results, we hypothesize that the reaction of *N*-sulfonyl-1,2,3-triazoles and *β*-enaminones might be controlled by the steric hindrance of the substituent on the α-position of amino. Under standard conditions, when a moderate steric group such as *n*-propyl or *n*-butyl was present at the amino α-position of *β*-enaminones, the reaction resulted in the formation of the corresponding products, namely imidazoles (**3r** and **3s**) and pyrroles (**5s** and **5t**), as depicted in Scheme 4a. In the synthesis of pyrroles, the presence of a methyl *p*-tolyl on the amino group resulted in a satisfactory yield of compounds **7a** and **7b** (72% and 85%, respectively; Scheme 4b).



Scheme 4. Further studies.

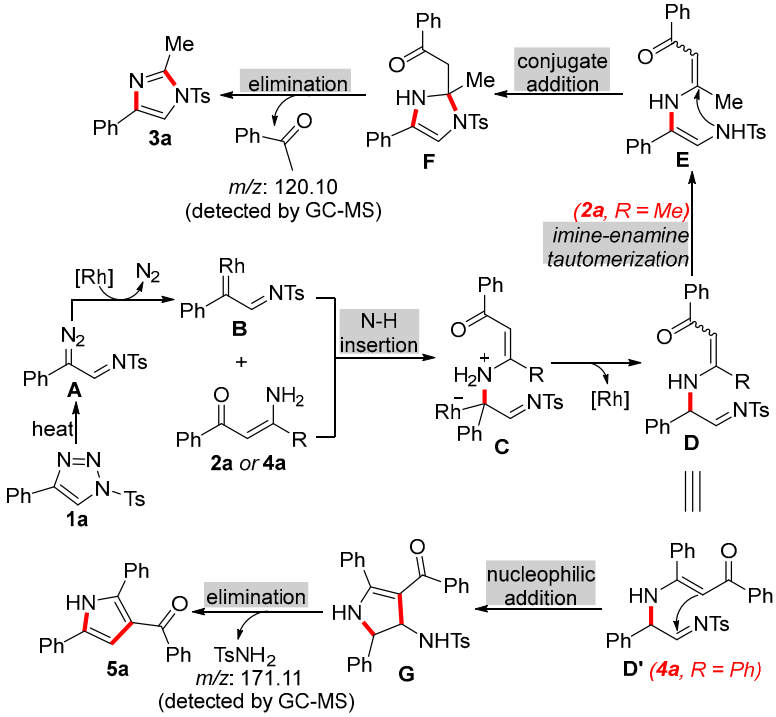
Notably, the reaction could be easily scaled up. As shown in Scheme 5, imidazole **3a** could be obtained with a satisfactory yield of 77% (1.44 g) when the scale of the reaction was increased to 5 mmol. Additionally, the 3,5-disubstituted pyrrole **5a** was obtained in a 75% yield (1.21 g) on the same scale. Subsequently, several transformations were performed to demonstrate the utility of the target products. The desulfonation of imidazole **3a** afforded the unprotected imidazole **8** in 96% yield (Scheme 5a). In addition, treating pyrrole **5a** with hydroxylamine hydrochloride and iodomethane successfully realized the formation of pyrrolyl oxime **9** in 94% yield (Scheme 5b). In the presence of sodium hydride, *N*-methylation between compound **5a** and iodomethane easily generated *N*-methylpyrrole derivative **10** in 95% yield (Scheme 5c). This highlights the synthetic utility of the current protocol.



Scheme 5. Gram-scale synthesis and further synthetic transformations.

The mechanism of this reaction was proposed as shown in Scheme 6 based on the above experimental results and previous reports [40–42]. *α*-Diazo imino intermediate **A**, which was generated from the ring-chain tautomerization of triazole **1a**, could be efficiently decomposed by the rhodium(II) catalyst to form *α*-imino rhodium carbene intermediate **B** along with the release of nitrogen gas. *β*-Enaminones (**2a** or **4a**) attacked the electrophilic carbene center of intermediate **B**, and 1,1-insertion occurred to convert intermediate **D** with the rhodium(II) catalyst regeneration. In the case where R was a methyl group, an imino–enamine tautomerization could be triggered, leading to the formation of a more stable intermediate **E**. This intermediate **E** then underwent an intramolecular 1,4-conjugate addition, resulting in the formation of intermediate **F**. The elimination of the intermediate **F** results in the desired product **3a**. In the case of **4a**, the phenyl group was bulky enough

to form the intermediate **D′**. Therefore, after the subsequent intramolecular nucleophilic addition and elimination processes, the corresponding product **5a** was obtained.



Scheme 6. Proposed mechanism for the formation of trisubstituted imidazoles and pyrroles.

3. Materials and Methods

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received. The solvents were purified and dried using standard procedures. The chromatography solvents were technical grade and distilled prior to use. The NMR spectra were recorded with a Bruker Avance 500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) with $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, and the coupling constants J are given in Hz (Supplementary Materials: ^{1}H NMR and ^{13}C NMR). HRMS spectra were obtained with an Agilent 6200 using a quadrupole time-of-flight mass spectrometer equipped with an ESI source. The melting points were measured using the SGWX-4 melting point apparatus and were not corrected. The X-ray source used for the single crystal X-ray diffraction analysis of compounds **3a** and **5a** was Mo Kα (λ = 0.71073 Å), and the thermal ellipsoid was drawn at the 30% probability level (Supplementary Materials: X-ray crystal data).

3.1. General Procedure for the Synthesis of Trisubstituted Imidazoles **3** *and Pyrroles* **5**

N-Sulfonyl-1H-1,2,3-triazoles **1** (0.2 mmol), β-enaminones **2** (0.2 mmol), and $Rh_2(oct)_4$ (2 mol%) were successively added to a Schlenk reaction tube. The reaction set was evacuated and backfilled with argon three times. Then, chlorobenzene (2.0 mL) was added to the reaction tube through a syringe. The reaction mixture was stirred vigorously in an oil bath preheated to 90 °C for 12 h. After the reaction was complete, the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, and then evaporated under a vacuum. The residue was purified by flash column chromatography on silica gel (200–300 mesh) using ethyl acetate and petroleum ether (1:8, v/v) as the elution solvents to give desired products **3** or **5**.

3.2. General Procedure for the Synthesis of Compound **8**

2-Methyl-4-phenyl-1-tosyl-1*H*-imidazole **3a** (0.15 mmol) and NaOH (2.25 mmol) were successively added to a Schlenk reaction tube. The reaction set was evacuated and backfilled with argon three times. Then, methanol (2.0 mL) was added into the reaction tube through a syringe. The reaction mixture was stirred vigorously in an oil bath preheated to 70 °C for 30 min. After the reaction was complete, the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, and then evaporated under a vacuum. The residue was purified by flash column chromatography on silica gel (200–300 mesh) using ethyl acetate and petroleum ether (1:3, *v/v*) as the elution solvents to give the desired product **8** in a 96% yield.

3.3. General Procedure for the Synthesis of Compound **9**

A mixture of (2,5-diphenyl-1*H*-pyrrol-3-yl)(phenyl)methanone **5a** (0.2 mmol), hydroxylamine hydrochloride (0.4 mmol), and sodium acetate (0.5 mmol) was added to a round-bottomed flask with a reflux condenser. Ethanol (4 mL) was then added, and the reaction mixture was stirred vigorously at reflux in an oil bath for 12 h. After quenching with water, the residue was extracted twice with ethyl acetate. The combined layer was washed with brine, dried over Na_2SO_4, and then evaporated under a vacuum. The residue was purified by flash column chromatography on silica gel (200–300 mesh) using ethyl acetate and petroleum ether (1:8, *v/v*) as the elution solvents to give the desired product **9** in a 94% yield.

3.4. General Procedure for the Synthesis of Compound **10**

NaH (60% in mineral oil, 0.5 mmol, 1.7 equiv.) was added to a solution of **5a** (0.25 mmol) in DCM (4 mL) at 0 °C in portions. After stirring for 5 min at 0 °C, MeI (0.22 mmol, 1.1 equiv.) was added dropwise, and the reaction mixture was allowed to warm to room temperature and stirred for another 19 h. After quenching with water, the residue was extracted twice with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4, filtrated and concentrated, and purified by column chromatography to afford **10** in 95% yield.

2-Methyl-4-phenyl-1-tosyl-1H-imidazole (**3a**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 96% yield (60 mg); mp 122–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 7.0 Hz, 2H), 7.67 (s, 1H), 7.39–7.35 (m, 4H), 7.25 (d, J = 7.5 Hz, 1H), 2.57 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 146.4, 141.0, 135.5, 132.7, 130.8, 129.1, 128.2, 127.8, 125.6, 114.4, 22.1, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O_2S$ 313.1005; found 313.1006.

2-Methyl-4-(p-tolyl)-1-tosyl-1H-imidazole (**3b**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 96% yield (62 mg); mp 60–62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.0 Hz, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 2.57 (s, 3H), 2.44 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 146.3, 141.0, 138.0, 135.4, 130.7, 129.9, 129.8, 127.7, 125.5, 113.9, 22.1, 21.7, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_2S$ 327.1162; found 327.1170.

4-(4-Ethylphenyl)-2-methyl-1-tosyl-1H-imidazole (**3c**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 95% yield (64 mg); mp 77–79 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.0 Hz, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.64 (q, J = 7.5 Hz, 2H), 2.57 (s, 3H), 2.42 (s, 3H), 1.23 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 146.3, 144.4, 141.0, 135.4, 130.8, 130.1, 128.6, 127.7, 125.5, 113.9, 29.1, 22.1, 15.9, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_2S$ 341.1318; found 341.1319.

4-(4-Methoxyphenyl)-2-methyl-1-tosyl-1H-imidazole (**3d**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 91% yield (62 mg); mp 66–68 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 9.0 Hz, 2H), 7.57 (s, 1H), 7.34 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H), 2.56 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 146.4, 146.3, 140.8, 135.4, 130.7, 127.7, 126.9, 125.5, 114.5, 113.2, 55.7, 22.1, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_3S$ 343.1111; found 343.1112.

4-(4-Fluorophenyl)-2-methyl-1-tosyl-1H-imidazole (**3e**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 94% yield (62 mg); mp 107–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.69 (dd, J = 8.5, 5.0 Hz, 2H), 7.61 (s, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 8.5 Hz, 2H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 246.3 Hz), 146.6, 146.5, 140.1, 135.3, 130.8, 129.0, 127.8, 127.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.6 Hz), 114.0, 22.1, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}FN_2O_2S$ 331.0911; found 331.0909.

4-(4-Chlorophenyl)-2-methyl-1-tosyl-1H-imidazole (**3f**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 94% yield (65 mg); mp 107–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.5 Hz, 2H), 7.66–7.65 (m, 3H), 7.36–7.32 (m, 4H), 2.56 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 146.6, 139.9, 135.2, 133.8, 131.3, 130.8, 129.2, 127.8, 126.8, 114.5, 22.1, 15.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}ClN_2O_2S$ 347.0616; found 347.0612.

4-(4-Bromophenyl)-2-methyl-1-tosyl-1H-imidazole (**3g**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 93% yield (72 mg); mp 104–106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.67 (s, 1H), 7.60 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 2.56 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.6, 139.9, 135.2, 132.2, 131.7, 130.8, 127.8, 127.1, 122.0, 114.6, 22.1, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}BrN_2O_2S$ 391.0110; found 391.0109.

4-(4-(tert-Butyl)phenyl)-2-methyl-1-tosyl-1H-imidazole (**3h**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 93% yield (68 mg); mp 69–71 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.0 Hz, 2H), 7.69–7.64 (m, 3H), 7.39 (d, J = 7.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 2.57 (s, 3H), 2.42 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 146.4, 146.4, 141.0, 135.5, 130.7, 129.9, 127.7, 126.0, 125.3, 114.0, 35.0, 31.7, 22.1, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{25}N_2O_2S$ 369.1631; found 369.1634.

2-Methyl-1-tosyl-4-(4-(trifluoromethyl)phenyl)-1H-imidazole (**3i**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 75% yield (57 mg); mp 76–78 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.82 (m, 4H), 7.76 (s, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 2.58 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 139.5, 136.2, 135.1, 130.9, 129.9 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.5, 127.9, 126.6, 126.1(q, $J_{C\text{-}F}$ = 3.8 Hz), 124.6(q, $J_{C\text{-}F}$ = 270.0 Hz), 115.6, 22.1, 15.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}F_3N_2O_2S$ 381.0879; found 381.0878.

2-Methyl-4-(4′-propyl-[1,1′-biphenyl]-4-yl)-1-tosyl-1H-imidazole (**3j**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in an 80% yield (69 mg); mp 94–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.79 (m, 4H), 7.71(s, 1H), 7.61 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.59 (s, 3H), 1.72–1.64 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 146.5, 142.4, 140.9, 140.7, 138.4, 135.4, 131.4, 130.8, 129.3, 127.8, 127.6, 127.1, 125.9, 114.3, 38.1, 25.0, 22.1, 15.6, 14.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{27}N_2O_2S$ 431.1788; found 431.1781.

2-Methyl-4-(m-tolyl)-1-tosyl-1H-imidazole (**3k**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 95% yield

(62 mg); mp 107–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.67 (s, 1H), 7.58 (s, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 2.57 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 146.4, 141.0, 138.8, 135.4, 132.5, 130.8, 129.0, 127.8, 126.2, 122.6, 114.3, 22.1, 21.8, 15.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_2S$ 327.1162; found 327.1163.

4-(3-Chlorophenyl)-2-methyl-1-tosyl-1H-imidazole (**3l**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in an 85% yield (59 mg); mp 83–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.73 (s, 1H), 7.68 (s, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 139.7, 135.1, 134.6, 130.8, 130.3, 128.1, 127.8, 125.7, 123.6, 115.0, 22.1, 15.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}ClN_2O_2S$ 347.0616; found 347.0625.

4-(3-Bromophenyl)-2-methyl-1-tosyl-1H-imidazole (**3m**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in an 82% yield (64 mg); mp 79–81 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.67 (s, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.39–7.35 (m, 3H), 7.22 (t, J = 8.0 Hz, 1H), 2.56 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.6, 139.5, 135.2, 134.8, 131.0, 130.8, 130.6, 128.6, 127.8, 124.1, 123.3, 115.0, 22.1, 15.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}BrN_2O_2S$ 391.0110; found 391.0119.

4-(2-Fluorophenyl)-2-methyl-1-tosyl-1H-imidazole (**3n**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 79% yield (52 mg); mp 57–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (t, J = 7.5 Hz, 1H), 7.85 (d, J = 4.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.23 (t, J = 7.0 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 10 Hz, 1H), 2.58 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2 (d, $J_{C\text{-}F}$ = 247.9 Hz), 146.5, 145.9, 135.4, 134.5, 130.8, 129.1 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.2 (d, $J_{C\text{-}F}$ = 3.6 Hz), 127.8, 124.7 (d, $J_{C\text{-}F}$ = 3.6 Hz), 120.6 (d, $J_{C\text{-}F}$ = 12.5 Hz), 118.4 (d, $J_{C\text{-}F}$ = 15.4 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.5 Hz), 22.1, 15.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}FN_2O_2S$ 331.0911; found 331.0914.

1-((4-Fluorophenyl)sulfonyl)-2-methyl-4-phenyl-1H-imidazole (**3o**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 91% yield (57 mg); mp 107–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97–7.94 (m, 2H), 7.73 (d, J = 7.5 Hz, 2H), 7.67 (s, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 8.0 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6 (d, $J_{C\text{-}F}$ = 257.5 Hz), 146.4, 141.3, 134.4 (d, $J_{C\text{-}F}$ = 2.8 Hz), 132.5, 130.7 (d, $J_{C\text{-}F}$ = 9.8 Hz), 129.1, 128.4, 125.6, 117.7 (d, $J_{C\text{-}F}$ = 22.9 Hz), 114.2, 15.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{14}FN_2O_2S$ 317.0755; found 317.0760.

1-((4-Bromophenyl)sulfonyl)-2-methyl-4-phenyl-1H-imidazole (**3p**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 76% yield (57 mg); mp 97–99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 9.0 Hz, 2H), 7.72 (t, J = 9.0 Hz, 4H), 7.65 (s, 1H), 7.38 (d, J = 7.5 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 141.4, 137.3, 133.6, 132.4, 130.6, 129.1, 129.1, 128.4, 125.6, 114.2, 15.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{14}BrN_2O_2S$ 376.9954; found 376.9952.

2-Ethyl-4-phenyl-1-tosyl-1H-imidazole (**3q**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 56% yield (37 mg); mp 49–51 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 7.0 Hz, 2H), 7.67 (s, 1H), 7.39-7.34 (m, 4H), 7.28 (d, J = 7.5 Hz, 1H), 2.90 (q, J = 7.5 Hz, 2H), 2.43 (s, 3H), 1.32 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 146.4, 140.9, 135.7, 132.9, 130.7, 129.0, 128.1, 127.7, 125.6, 114.3, 22.4, 22.1, 12.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_2S$ 327.1162; found 327.1163.

4-Phenyl-2-propyl-1-tosyl-1H-imidazole (**3r**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a colorless oil in a 45% yield (31 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 7.0 Hz, 2H), 7.66 (s, 1H), 7.38–7.33 (m, 4H), 7.27 (t, J = 7.5 Hz, 1H), 2.85 (t, J = 7.5 Hz, 2H), 2.43 (s, 3H), 1.81–1.74 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 146.4, 141.0, 135.8, 132.9, 130.7, 129.0, 128.1, 127.6, 125.6, 114.3, 30.8, 22.1, 21.9, 14.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_2S$ 341.1318; found 341.1312.

2-Butyl-4-phenyl-1-tosyl-1H-imidazole (**3s**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a colorless oil in a 44% yield (31 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 7.5 Hz, 2H), 7.67 (s, 1H), 7.38–7.33 (m, 4H), 7.28 (d, J = 7.5 Hz, 1H), 2.87 (t, J = 8 Hz, 2H), 2.43 (s, 3H), 1.72–1.69 (m, 2H), 1.42–1.37 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 146.4, 140.9, 135.7, 132.9, 130.7, 129.1, 128.2, 127.7, 125.6, 114.3, 30.5, 28.6, 22.9, 22.1, 14.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_2S$ 355.1475; found 355.1482.

(2,5-Diphenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5a**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 91% yield (59 mg); mp 81–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.80 (d, J = 7.0 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.45-7.42 (m, 3H), 7.39 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.29–7.24 (m, 4H), 6.84 (d, J = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 139.8, 138.3, 132.3, 132.1, 131.8, 130.1, 129.5, 128.9, 128.8, 128.5, 128.3, 127.5, 124.5, 122.3, 110.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{18}NO$ 324.1383; found 324.1382.

Phenyl(2-phenyl-5-(p-tolyl)-1H-pyrrol-3-yl)methanone (**5b**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 91% yield (61 mg); mp 81–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.47–7.38 (m, 5H), 7.31 (t, J = 7.7 Hz, 2H), 7.21–7.17 (m, 5H), 6.78 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 139.8, 138.1, 137.3, 132.5, 132.2, 132.1, 130.1, 130.1, 129.1, 128.9, 128.7, 128.4, 128.3, 124.6, 122.2, 110.4, 21.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{20}NO$ 338.1539; found 338.1545.

(5-(4-Ethylphenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5c**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 92% yield (64 mg); mp 71–73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.80 (d, J = 7.0 Hz, 2H), 7.47-7.42 (m, 5H), 7.32 (t, J = 7.5 Hz, 2H), 7.26–7.22 (m, 5H), 6.81 (d, J = 3.0 Hz, 1H), 2.67 (q, J = 7.5 Hz, 2H), 1.26 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 143.8, 139.8, 138.0, 132.5, 132.2, 132.1, 130.1, 129.3, 128.9, 128.9, 128.7, 128.4, 128.3, 124.6, 122.2, 110.4, 29.0, 15.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{22}NO$ 352.1693; found 352.1689.

(5-(4-Methoxyphenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5d**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 92% yield (65 mg); mp 111–113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 7.0 Hz, 3H), 7.31 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 3H), 6.92 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 3.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 159.3, 139.9, 137.9, 132.4, 132.3, 132.1, 130.1, 128.9, 128.7, 128.3, 128.3, 126.0, 124.8, 122.2, 114.9, 109.8, 55.8; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{20}NO$ 354.1489; found 354.1489.

(5-(4-Fluorophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5e**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 85% yield (58 mg); mp 104–106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.78 (d, J = 7.0 Hz, 2H), 7.50 (dd, J = 9.0, 5.0 Hz, 2H), 7.45–7.41 (m, 3H), 7.31 (t, J = 7.5 Hz, 2H), 7.24–7.22 (m, 3H), 7.08 (t, J = 8.5 Hz, 2H), 6.76 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 162.4 (d, $J_{C\text{-}F}$ = 245.0 Hz), 139.7, 138.3, 132.2, 132.1, 131.5, 130.1,

128.8 (d, J_{C-F} = 6.3 Hz), 128.6, 128.3, 128.2, 126.4, 126.3, 122.4, 116.5 (d, J_{C-F} = 22.5 Hz), 110.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{17}FNO$ 342.1289; found 342.1287.

(5-(4-Chlorophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5f**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 84% yield (60 mg); mp 112–114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.77 (d, *J* = 7.0Hz, 2H), 7.46–7.42 (m, 3H), 7.39 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.35–7.30 (m, 4H), 7.23–7.19 (m, 3H), 6.79 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 139.6, 138.6, 133.1, 132.2, 131.9, 131.3, 130.4, 130.1, 129.6, 128.9, 128.8, 128.6, 128.3, 125.8, 122.4, 111.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{17}ClNO$ 358.0993; found 358.1002.

(5-(4-Bromophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5g**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 84% yield (67 mg); mp 127–129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.46–7.43 (m, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29-7.27 (m, 3H), 6.85 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 139.6, 138.7, 132.5, 132.3, 131.9, 131.3, 130.8, 130.1, 128.9, 128.7, 128.6, 128.3, 126.1, 122.4, 121.1, 111.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{17}BrNO$ 402.0488; found 402.0489.

(5-(4-(tert-Butyl)phenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5h**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 93% yield (70 mg); mp 98–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.49–7.40 (m, 7H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.28–7.23 (m, 3H), 6.82 (s, 1H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 150.7, 139.8, 138.0, 132.4, 132.3, 132.1, 130.1, 129.1, 128.9, 128.8, 128.4, 128.3, 126.4, 124.3, 122.3, 110.5, 35.0, 31.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{26}NO$ 380.2009; found 380.2008.

Phenyl(2-phenyl-5-(4′-propyl-[1,1′-biphenyl]-4-yl)-1H-pyrrol-3-yl)methanone (**5i**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 85% yield (72 mg); mp 149–151 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.59 (s, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.41–7.36 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.20–7.15 (m, 3H), 6.85 (d, *J* = 3.0 Hz, 1H), 2.64 (d, *J* = 8.0 Hz, 2H), 1.69 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 142.5, 140.0, 139.8, 138.7, 138.2, 132.3, 132.2, 132.1, 130.5, 130.2, 129.4, 129.0, 128.7, 128.4, 128.3, 127.8, 127.1, 125.0, 122.3, 110.9, 38.1, 25.0, 14.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{28}NO$ 442.2165; found 442.2170.

Phenyl(2-phenyl-5-(m-tolyl)-1H-pyrrol-3-yl)methanone (**5j**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 86% yield (58 mg); mp 118–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 6.0 Hz, 3H), 7.37–7.31 (m, 4H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 6.0 Hz, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 139.8, 139.0, 138.4, 132.5, 132.2, 132.1, 131.8, 130.1, 129.3, 128.9, 128.7, 128.4, 128.3, 125.4, 122.2, 121.7, 110.8, 21.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{20}NO$ 338.1539; found 338.1531.

(5-(3-Chlorophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5k**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 85% yield (60 mg); mp 83–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.51 (s, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.41–7.38 (m, 3H), 7.34–7.27 (m, 3H), 7.23–7.18 (m, 4H), 6.80 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 139.6, 138.9, 135.4, 133.6, 132.3, 131.8, 130.9, 130.6, 130.1, 128.9, 128.7, 128.6, 128.4, 127.3, 124.6, 122.6, 122.3, 111.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{17}ClNO$ 358.0993; found 358.0992.

(5-(3-Bromophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5l**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow

solid in an 87% yield (69 mg); mp 99–101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.78 (d, J = 7.0 Hz, 2H), 7.67 (s, 1H), 7.46–7.40 (m, 4H), 7.37 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.25–7.21 (m, 4H), 6.81 (d, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 139.6, 138.9, 133.9, 132.3, 131.8, 130.9, 130.7, 130.2, 130.1, 128.9, 128.8, 128.7, 128.4, 127.4, 123.6, 123.1, 122.4, 111.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{17}BrNO$ 402.0488; found 402.0489.

(5-(2-Fluorophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**5m**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 79% yield (54 mg); mp 77–79 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.81 (d, J = 7.0 Hz, 2H), 7.64 (t, J = 8.0 Hz, 1H), 7.48–7.44 (m, 3H), 7.34 (t, J = 8.0 Hz, 2H), 7.29–7.26 (m, 3H), 7.23–7.13 (m, 3H), 6.98 (d, J = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ192.8, 159.2 (d, $J_{C\text{-}F}$ = 124.1 Hz), 139.7, 138.3, 132.2, 132.0, 130.1, 128.8, 128.6, 128.57 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.4, 127.3 (d, $J_{C\text{-}F}$ = 4.0 Hz), 127.1, 125.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 121.7, 119.4, 119.3, 116.8 (d, $J_{C\text{-}F}$ = 23.8 Hz), 112.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{17}FNO$ 342.1289; found 342.1281.

(4-Chlorophenyl)(2-(4-chlorophenyl)-5-phenyl-1H-pyrrol-3-yl) methanone (**5n**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 75% yield (58 mg); mp 94–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.77 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 7.0 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.34 (m, 4H), 6.80 (d, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.2, 138.7, 138.0, 136.8, 134.8, 132.7, 131.4, 130.5, 130.0, 129.6, 129.2, 128.8, 127.9, 124.6, 122.3, 110.8; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{16}Cl_2NO$ 392.0603; found 392.0612.

(2,5-Diphenyl-1H-pyrrol-3-yl) (naphthalen-2-yl) methanone (**5o**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 92% yield (68 mg); mp 107–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.34 (s, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.83 (t, J = 8.0 Hz, 3H), 7.60–7.52 (m, 5H), 7.49 (d, J = 7.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.31–7.26 (m, 3H), 7.22 (d, J = 7.5 Hz, 1H), 6.92 (d, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 138.1, 137.0, 135.4, 132.7, 132.3, 132.2, 131.8, 131.7, 129.7, 129.5, 128.9, 128.8, 128.6, 128.2, 128.2, 128.1, 127.6, 126.8, 126.1, 124.5, 122.6, 111.0; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{20}NO$ 374.1539; found 374.1537.

(2,5-Diphenyl-1H-pyrrol-3-yl) (thiophen-2-yl) methanone (**5p**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 90% yield (59 mg); mp 86–88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.66 (d, J = 3.5 Hz, 1H), 7.60–7.54 (m, 5H), 7.42 (t, J = 8.0 Hz, 2H), 7.36 (t, J = 7.0 Hz, 2H), 7.33–7.28 (m, 2H), 7.04 (dd, J = 5.0, 4.0 Hz, 1H), 6.99 (d, J = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1, 145.9, 137.4, 134.1, 133.2, 132.4, 132.1, 131.8, 129.5, 129.0, 128.7, 128.6, 128.0, 127.6, 124.6, 122.3, 110.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{16}NOS$ 330.0947; found 330.0955.

(2-Isopropyl-5-phenyl-1H-pyrrol-3-yl) (phenyl)methanone (**5q**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 86% yield (50 mg); mp 85–87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.84 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.0 Hz, 1H), 7.48–7.44 (m, 4H), 7.36 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 6.64 (d, J = 3.0 Hz, 1H), 3.87 (m, 1H), 1.37 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 147.8, 141.1, 132.2, 131.6, 129.8, 129.5, 129.4, 128.5, 127.2, 124.3, 120.2, 110.1, 26.8, 22.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{20}NO$ 290.1539; found 290.1530.

Phenyl(5-phenyl-2-propyl-1H-pyrrol-3-yl) methanone (**5r**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 42% yield (24 mg); mp 74–76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.87–7.82 (m, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.49–7.44 (m, 4H), 7.39–7.34 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 3.0 Hz, 1H), 3.02 (t, J = 7.5 Hz, 2H), 1.76 (m, 2H), 1.60 (s, 3H), 1.01 (t,

J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 142.4, 141.0, 132.1, 131.6, 130.0, 129.5, 129.4, 128.5, 127.1, 124.2, 121.2, 109.8, 30.1, 23.1, 14.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{20}NO$ 290.1539; found 290.1542.

(2-Butyl-5-phenyl-1H-pyrrol-3-yl) (phenyl)methanone (**5s**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in a 49% yield (30 mg); mp 74–76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.55–7.45 (m, 5H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 3.01 (t, *J* = 7.5 Hz, 2H), 1.7–1.64 (m, 2H), 1.39–1.32 (m, 2H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 142.7, 140.7, 131.8, 131.3, 129.8, 129.1, 129.0, 128.1, 126.6, 123.9, 120.6, 109.4, 31.7, 27.5, 22.6, 14.0, 13.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{22}NO$ 304.1696; found 304.1702.

(1,2-Dimethyl-5-phenyl-1H-pyrrol-3-yl) (phenyl)methanone (**7a**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 72% yield (40 mg); mp 96–98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.0 Hz, 2H), 7.26 (t, *J* = 7.5Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.04 (q, *J* = 8.0 Hz, 4H), 6.98 (d, *J* = 6.5 Hz, 1H), 6.64 (s, 1H), 3.62 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.4, 140.0, 135.8, 135.6, 131.9, 130.2, 128.8, 128.2, 128.0, 126.2, 125.9, 120.2, 120.1, 34.2, 11.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{18}NO$ 276.1383; found 276.1388.

1-(2-Methyl-5-phenyl-1-(p-tolyl)-1H-pyrrol-3-yl) ethan-1-one (**7b**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow solid in an 85% yield (49 mg); mp 66–68 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 4.0 Hz, 4H), 7.32–7.27 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.64 (s, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 138.5, 136.6, 136.5, 135.8, 130.3, 129.7, 128.7, 127.2, 126.6, 126.4, 122.8, 121.1, 31.5, 21.5, 13.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{20}NO$ 290.1539; found 290.1538.

2-Methyl-4-phenyl-1H-imidazole (**8**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) to afford a white solid in a 96% yield (30 mg); mp 57–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.0 Hz, 2H), 7.37 (s, 1H), 7.30 (t, *J* = 7.5Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 3.39 (brs, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.7, 138.2, 133.2, 129.1, 127.2, 125.1, 115.6, 14.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2$ 159.0917; found 159.091.

(E)-(2,5-Diphenyl-1H-pyrrol-3-yl) (phenyl)methanone oxime (**9**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a white solid in a 94% yield (63 mg); mp 95–97 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.44 (s, 1H), 11.19 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 4H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.26–7.23 (m, 5H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.7, 137.7, 133.2, 132.8, 131.6, 129.6, 129.5, 129.1, 129.0, 128.8, 127.4, 127.2, 127.0, 126.5, 124.8, 115.1, 109.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{19}N_2O$ 339.1492; found 339.1496.

(1-Methyl-2,5-diphenyl-1H-pyrrol-3-yl) (phenyl)methanone (**10**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a colorless oil in a 98% yield (66 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.40–7.35 (m, 5H), 7.34 (s, 1H), 7.32–7.27 (m, 3H), 6.67 (s, 1H), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 140.8, 140.1, 135.7, 132.9, 132.3, 131.6, 131.2, 129.8, 129.4, 129.0, 128.6, 128.5, 128.1, 128.1, 122.3, 112.3, 34.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{20}NO$ 338.1539; found 338.1544.

4. Conclusions

In conclusion, we have demonstrated that the Rh(II)-catalyzed substituent-controllable regioselective annulations provide a new synthetic strategy for trisubstituted imidazoles and pyrroles. The highlight of the current reaction is the substituent-dependent product

selectivity. The imidazole skeleton was formed via N-H insertion to α-imino rhodium carbene, followed by intramolecular 1,4-conjugate addition when α-carbon atom of the amino group bore with methyl. Switching the methyl to phenyl group, the pyrrole framework was generated through N-H insertion and the intramolecular nucleophilic addition process. The large-scale reactions and transformations of the products further demonstrated the potential synthetic value of this strategy.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules28114416/s1, Characterization data for products **3** **5**, **7**, **8**, **9**, and **10** including ^{1}H- and ^{13}C-NMR spectroscopies, are available online. CCDC 2260879 and 2260880 contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

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