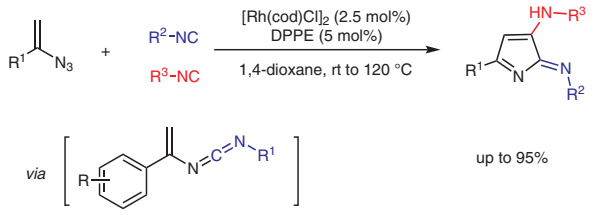
Synthesis Y. Wang et al. Paper

Rhodium-Catalyzed Double Isocyanide Insertion via a Vinylcarbodiimide Intermediate for the Synthesis of 2*H*-Pyrrol-2-imines

Yunlong Wang[a]
Zongyang Li[b]
Haiying Zhao*[a]
Zhenhua Zhang*[b]

[a] Inner Mongolia Key Laboratory of Fine Organic Synthesis, College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China
hyzhao@imu.edu.cn
[b] Department of Applied Chemistry, China Agricultural University, West Yuanmingyuan Rd. 2, Beijing 100193, P. R. of China
zhangzhh@cau.edu.cn



Received: 29.03.2019
Accepted after revision: 24.04.2019
Published online: 21.05.2019
DOI: 10.1055/s-0037-1611830; Art ID: ss-2019-f0057-op

Abstract 2*H*-Pyrrol-2-imine is an important structural motif exhibiting in biologically active compounds and natural products. An efficient rhodium-catalyzed one-pot reaction of one vinyl azide with sequentially with two different isocyanides is reported, which offers an alternative facile access to 3-amino-5-aryl-2*H*-pyrrol-2-imines bearing various substitution on the nitrogens in good yields. An unstable vinylcarbodiimide is the key intermediate in this cascade reaction.

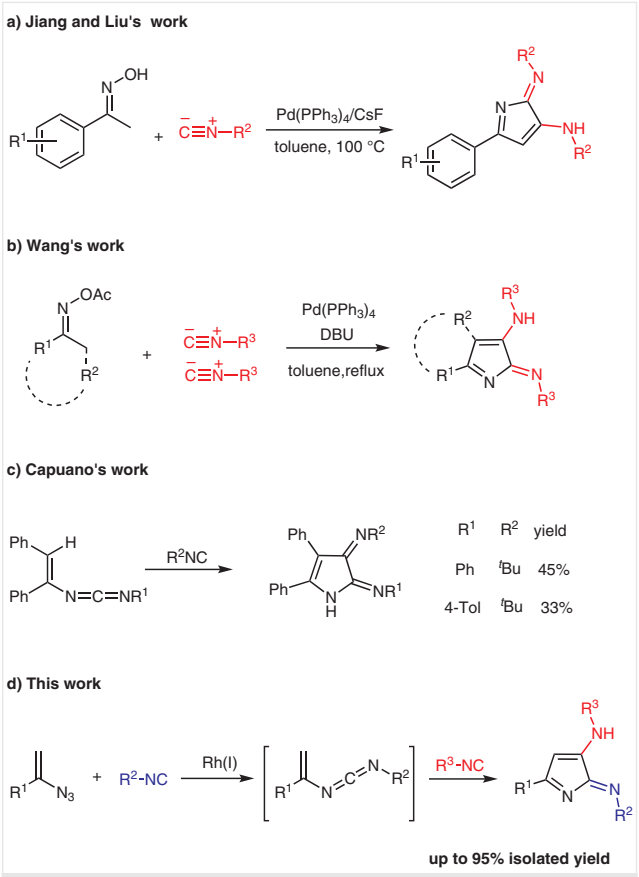
Key words vinyl azide, vinylcarbodiimide, 2*H*-pyrrol-2-imine, isocyanide, palladium catalysis

2*H*-Pyrrole is an important structural motif present in a broad range of biologically active compounds and natural products,[1] in which 2*H*-pyrrol-2-imines possess versatile applications.[2] One strategy to access this aza-five-member ring is based on the reaction of oximes with two isocyanides, which was reported by two different research groups in 2017. Jiang, Liu, and co-workers reported a redox-neutral palladium-catalyzed N–O/C(sp^3)–H functionalization of one molecule of an aryl oxime with two molecules of an isocyanide to give a 2*H*-pyrrol-2-imine (Scheme 1a).[3] Wang and co-workers also reported a palladium-catalyzed N–O cleavage of *O*-acetyl oximes with double isocyanide insertion to obtain 2*H*-pyrrol-2-imines (Scheme 1b).[4] However, the two isocyanides in these transformations must be the same. In 1988, Capuano and co-workers presented several examples of 2*H*-pyrrol-2-imines synthesis via the cyclization of vinylcarbodiimides with isocyanides that had different nitrogen-substituted groups (Scheme 1c).[5] Nevertheless, the lack of convenient access to vinylcarbodiimides and their instability in isolation and storage limit its further development.

Organic azides have been developed as a convenient precursor to N-containing cycles.[6] The transition-metal-catalyzed reaction of an azide with σ-donor/π-acceptor isocyanides has also shown value in the facile access to carbodiimide intermediates.[7] In 2018, we reported a Rh(I)-catalyzed coupling reaction of vinyl azides with isocyanides at the azide moiety to form active vinylcarbodiimides, which gives a new ladder to aza-six-member rings.[7h] Following this work, herein we reported a highly efficient one-pot Rh(I)-catalyzed transformation of vinyl azides with two different isocyanides to synthesize 2*H*-pyrrol-2-imines with different *N*-substituted groups.

At the outset, the reaction of (1-azidovinyl)benzene (**1a**), 1-chloro-4-isocyanobenzene (**2a**), and *tert*-butyl isocyanide (**3a**) was selected as a model. Firstly, **1a** was reacted with 1.07 equiv of isocyanide **2a** in the presence of catalyst $[Rh(cod)Cl]_2$ in 1,4-dioxane at room temperature; after 4 hours, when **1a** had been consumed, another isocyanide **3a** was added and the mixture was heated to 120 °C for 40 minutes. To our delight, this process was amenable to the selective and sequential installation of two different isocyanides and the corresponding cross *N*-substituted 2*H*-pyrrol-2-imine **4aa** was obtained in 61% yield (Table 1, entry 2). In addition, no product was obtained in the absence of Rh catalyst and ligand (Table 1, entry 1). In further optimization of the conditions, we found that phosphine ligands improved the yield; the addition of PPh_3 ligand gave **4aa** in 90% yield (Table 1, entry 3) and different bidentate phosphine ligands with different bite angles had different effects (Table 1, entries 4–7). The best yield of **4aa** was obtained using DPPE as the ligand.

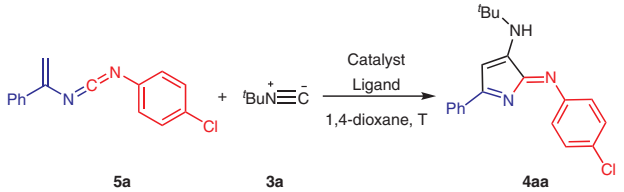
In one-pot reactions, the conditions need to be suitable for not only the first coupling step, but also the second cyclization step. Screening the conditions for the cyclization of isolated vinylcarbodiimide **5a** with *tert*-butyl isocyanide



Scheme 1 Approaches to *N*-substituted 2*H*-pyrrol-2-imines

(**3a**) showed that temperature is the key, and Rh catalysts/phosphine ligands are not necessary (Table 2). Furthermore, the use of DPPM, DPPE, and 10 mol% of PPh_3 decreased the yields.

Table 2 Optimization of the Cyclization Reaction of a Vinylcarbodiimide with *tert*-Butyl Isocyanide[a]

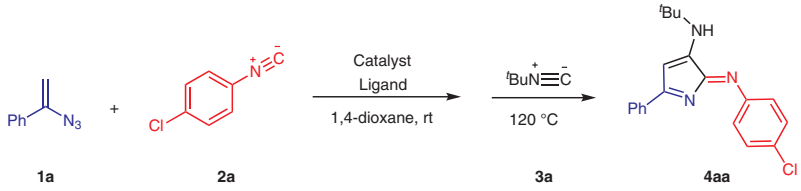


5a **3a** **4aa**

Entry	Catalyst (mol%)	Ligand (mol%)	T (°C)	Yield[b] (%)
1	–	–	rt	52
2	–	–	120	>95
3	$[Rh(cod)Cl]_2$ (2.5)	–	rt	58
4	$[Rh(cod)Cl]_2$ (2.5)	–	120	>95
5	$[Rh(cod)Cl]_2$ (2.5)	PPh_3 (5)	120	>95
6	$[Rh(cod)Cl]_2$ (2.5)	PPh_3 (10)	120	85
7	$[Rh(cod)Cl]_2$ (2.5)	DPPM (5)	120	88
8	$[Rh(cod)Cl]_2$ (2.5)	DPPE (5)	120	>95
9	$[Rh(cod)Cl]_2$ (2.5)	DPPP (5)	120	81
10	$[Rh(cod)Cl]_2$ (2.5)	Xantphos (5)	120	>95

[a] Reaction conditions: **5a** (0.15 mmol), **3a** (0.18 mmol), catalyst/ligand, 1,4-dioxane (2 mL), rt, 3 h or 120 °C, 40 min.
[b] Isolated yield.

Table 1 Optimization of the Rh-Catalyzed One-Pot Reaction of a Vinyl Azide Sequentially with Two Different Isocyanides[a]



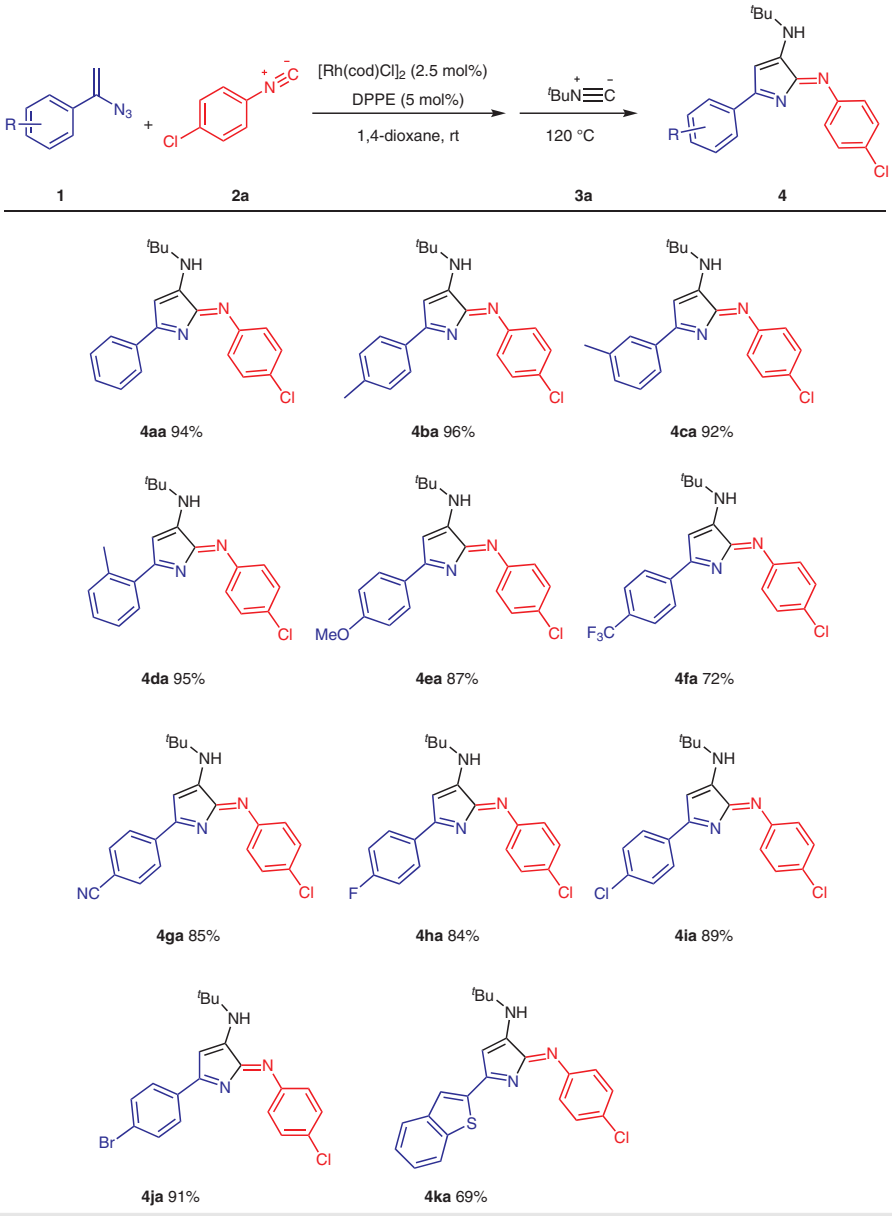
1a **2a** **3a** **4aa**

Entry	Catalyst (mol%)	Ligand (mol%)	Yield[b] (%)
1	–	–	n.r.
2	$[Rh(cod)Cl]_2$ (2.5)	–	61
3	$[Rh(cod)Cl]_2$ (2.5)	PPh_3 (5)	90
4	$[Rh(cod)Cl]_2$ (2.5)	DPPM (5)	61
5	$[Rh(cod)Cl]_2$ (2.5)	DPPE (5)	94
6	$[Rh(cod)Cl]_2$ (2.5)	DPPP (5)	75
7	$[Rh(cod)Cl]_2$ (2.5)	Xantphos (5)	78

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.16 mmol), catalyst/ligand, 1,4-dioxane (2 mL), rt until complete consumption of **1a**, then addition of **3a** (0.18 mmol), 120 °C, 40 min.
[b] Isolated yield. DPPM = bis(diphenylphosphino)methane. DPPP = 1,3-bis(diphenylphosphino)propane. DPPE = 1,2-bis(diphenylphosphino)ethane. Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

With the optimized reaction conditions described above, an array of functionalized aryl-substituted vinyl azides **1a–k** were subjected to this reaction first with 1-chloro-4-isocyanobenzene (**2a**) and then with *tert*-butyl isocyanide (**3a**) in order to investigate the generality (Scheme 2). As expected, the reaction showed excellent substrate scope. The steric hindrance of substituent at different positions has little adverse impact on the reactivity (**4ba**, **4ca**, **4da**, 92–96% yield). 1-Arylvinyl azides with different electron-withdrawing/electron-donating groups on the aryl substituent, such as MeO, F_3C, and NC, also gave excellent isolated yields of products (**4ea**, **4fa**, **4ga**, 72–87% yield). In addition, halogen substituents were well-tolerated on the aryl ring (**4ha**, **4ia**, **4ja**, 84–91% yield), thus offering an opportunity for further cross-coupling, as well as facilitating the expedient synthesis. Furthermore, the use of 1-benzothiophen-2-ylvinyl azide as the substrate gave the corresponding product **4ka** in 69% yield.

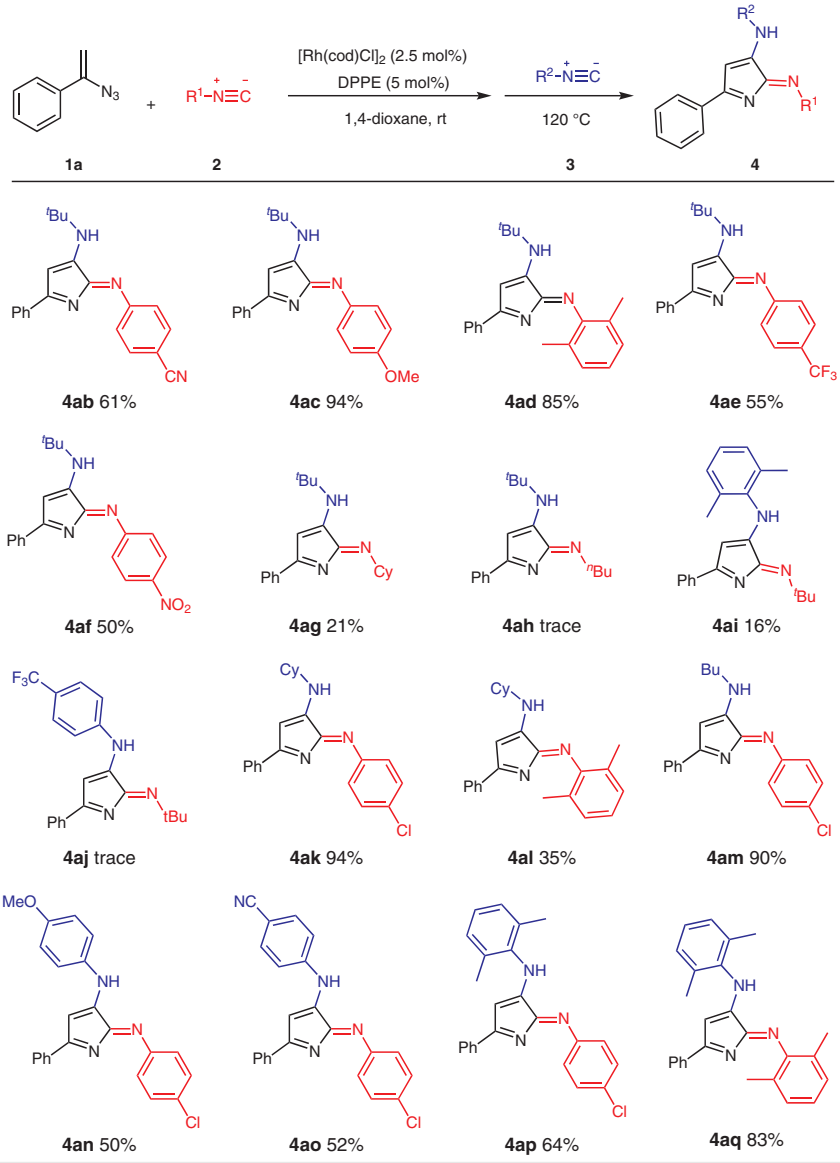
To further explore the diversity of products generated by this reaction, the generality of different isocyanides was investigated and the results are presented in Scheme 3. For the first isocyanide, all of different substituted aryl isocya-



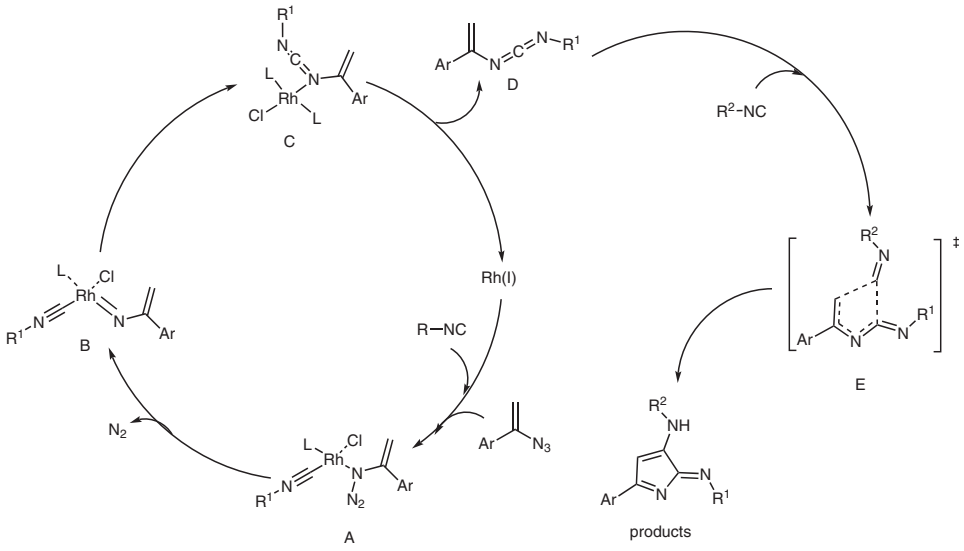
Scheme 2 Substrate generality of 1-arylvinyl azides. *Reagents and conditions*: **1** (0.15 mmol), **2a** (0.16 mmol), $[Rh(cod)Cl]_2$ (2.5 mol%), DPPE (5 mol%), 1,4-dioxane (2 mL), rt until complete consumption of **1**, then addition of **3a** (0.18 mmol), 120 °C, 40 min; all yields are isolated yields.

nides used gave 2*H*-pyrrol-2-imine derivatives (**4aa**–**4af**). Electron-donating aryl isocyanides such as **2c** (R^2 = 4-$MeOC_6H_4$) gave compound **4ac** in 94% yield, the electron-withdrawing aryl isocyanides such as **2e** (R^2 = 4-$F_3CC_6H_4$) and **2f** (R^2 = 4-$NO_2C_6H_4$) gave compounds **4ae** and **4af**, respectively, in moderate yields (55% and 50%), However, when alkyl isocyanides were used as the first isocyanide, R^1 = Cy, Bu, and ^{t}Bu, the corresponding 2*H*-pyrrol-2-imines **4ag**, **4ah**, **4ai**, **4aj** were obtained only in low yields. According to our previous study,[7h] the reaction of vinyl azides with alkyl isocyanides could well produce 1-alkyl-3-vinylcarbodiimides. We have also tried to use isolated 1-alkyl-3-vinylcarbodiimides in the second step of the reaction with isocyanides, but the yields of 2*H*-pyrrol-2-imine were still <30%. These results showed that 1-alkyl-3-vinylcarbodiimides were unsuitable for the cyclization with isocyanide.

To our delight, when the first isocyanide was an aryl isocyanide (via 1-aryl-3-vinylcarbodiimides), regardless of whether the second isocyanide was an alkyl isocyanide or aryl isocyanide, the reactions all gave 2*H*-pyrrol-2-imine products in moderate to high yields (**4ak**–**4ap**), Furthermore, we also utilized the same isocyanide for both steps and obtained 2*H*-pyrrol-2-imine derivatives **4aq** (83% yield) and **4ar** (45% yield).



Scheme 3 Substrate generality of isocyanides. *Reagents and conditions*: **1a** (0.15 mmol), **2** (0.16 mmol), $[Rh(cod)Cl]_2$ (2.5 mol%), DPPE (5 mol%), 1,4-dioxane (2 mL), rt until complete consumption of **1a** then addition of **3** (0.18 mmol), 120 °C, 40 min; all yields are isolated yields.



Scheme 4 Plausible mechanism

A plausible mechanism for the one-pot sequential reaction of vinyl azide with two different isocyanides is shown in Scheme 4, which generally involves two processes including Rh(I)-catalyzed cross-coupling of vinyl azide with the first isocyanide, and the cyclization of the vinylcarbodiimide intermediate with the second isocyanide. Initially, the key intermediate vinylcarbodiimide **D** is generated via a Rh–nitrene pathway with only release of N_2. Next, the thermal cyclization of the second isocyanide gives the 2*H*-pyrrol-2-imine as the product. According to the condition screening in Table 2, which could also be considered as controlled experiments, the cyclization does not go through a Rh(I)-mediated pathway, and isocyanide reacted with vinyl azide prior to the vinylcarbodiimide.

In summary, we have reported an efficient rhodium-catalyzed one-pot reaction of one vinyl azide with two sequential isocyanides, which offers an alternative facile approach to cross *N*-substituted 2*H*-pyrrol-2-imines in good yields. In addition, this transformation also features good functional group tolerance. From the perspective of the reaction pathway, the unstable vinylcarbodiimide is the key intermediate in this cascade reaction. The further applications of 2*H*-pyrrol-2-imines are currently underway in our laboratories.

All reactions were performed in a glass vial under N_2 atmosphere. Anhydrous solvents were distilled on a small scale with CaH_2 or Na and stored under N_2. Petroleum ether bp 60–90 °C (PE) was used. For chromatography, 200–300 mesh silica gel (Qingdao, China) was employed. ^{1}H and ^{13}C NMR spectra were recorded on Varian 300 or Varian Mercury 400 spectrometer in $CDCl_3$ referenced to TMS (^{1}H δ = 0; ^{13}C δ = 77.00) or in DMSO-d_6 referenced to residual DMSO-d_5 (^{1}H δ = 2.50; ^{13}C δ = 39.52). IR spectra were recorded with a Nicolet AVATAR 330 FT-IR spectrophotometer. Mass spectra were obtained on a Waters Auto Purification LC/MS system. HRMS were obtained on a Bruker Apex IV FTMS spectrometer. All catalysts and ligands were purchased from Sigma-Aldrich. All alkyl and aryl isocyanides and aryl isocyanides are commercially available, unless stated otherwise.

N-tert-Butyl-2-[(4-chlorophenyl)imino]-5-phenyl-2*H*-pyrrol-3-amine (4aa); Typical Procedure

To a dry 5-mL tube equipped with a magnetic stir bar, $[Rh(cod)Cl]_2$ (1.8 mg, 0.004 mmol), and DPPE (3 mg, 0.008 mmol) was added to freshly distilled 1,4-dioxane (2 mL). The tube was sealed, evacuated and refilled with N_2. Then, vinyl azide **1a** (22 mg, 0.15 mmol) and isocyanide **2a** (22 mg, 0.16 mmol) were added and the mixture was stirred at rt until **1a** disappeared (TLC monitoring). Then 0.1 M *t*-BuNC (**3a**) in 1,4-dioxane (15 mg, 0.18 mmol) was added and the mixture was stirred at 120 °C for 40 min. When the reaction was complete, the mixture was concentrated under reduced pressure. The resulting crude residue was purified via column chromatography (silica gel, PE/EtOAC 30:1) to afford the desired product **4aa** (48 mg, 94%).

(1-Azidovinyl)benzene (1a); Typical Procedure[7h]

In a flask with a magnetic bar, Ag_2CO_3 (0.2 mmol) was suspended in DMSO (4 ml). Phenylacetylene (2 mmol), $TMSN_3$ (4 mmol), and H_2O (4 mmol) were added to flask, respectively. Then the mixture was heat to 80 °C. After 1 h, the mixture was partitioned between Et_2O and H_2O, and the organic phase was separated, dried (Na_2SO_4), and concentrated. The residue was chromatographed (PE) to afford (1-azidovinyl)benzene (**1a**); yield: 232 mg (1.6 mmol, 80%).

N-tert-Butyl-2-[(4-chlorophenyl)imino]-5-phenyl-2*H*-pyrrol-3-amine (4aa)

Following the typical procedure gave the product as a dark red solid; yield: 47 mg (94%).

IR (neat): 3353, 2975, 2930, 1629, 1607, 1576, 1508, 1455, 1422, 1354, 1228, 842, 728 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.4 Hz, 2 H), 7.75 (dd, *J* = 8.8, 2.1 Hz, 2 H), 7.55–7.44 (m, 4 H), 7.35 (dd, *J* = 8.8, 2.1 Hz, 2 H), 6.27 (s, 1 H), 5.71 (s, 1 H), 1.46 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.94, 165.09, 155.43, 145.61, 133.98, 132.77, 131.97, 128.89, 128.61, 127.93, 89.64, 52.47, 28.70.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}ClN_3$: 338.1419; found: 338.1403.

N-*tert*-Butyl-2-[(4-chlorophenyl)imino]-5-(*p*-tolyl)-2*H*-pyrrol-3-amine (4ba)

Following the typical procedure gave the product as a dark red solid; yield: 51 mg (96%).

IR (neat): 3351, 2972, 2926, 1628, 1596, 1572, 1346, 1227, 1089, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.1 Hz, 2 H), 7.74 (d, *J* = 8.7 Hz, 2 H), 7.34 (d, *J* = 8.7 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 5.70 (s, 1 H), 2.42 (s, 3 H), 1.46 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.82, 165.30, 155.23, 145.76, 143.69, 131.79, 131.24, 129.39, 129.09, 128.78, 127.92, 89.58, 52.38, 28.69, 21.99.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}ClN_3$: 352.1575; found: 352.1560.

N-*tert*-Butyl-2-[(4-chlorophenyl)imino]-5-(*m*-tolyl)-2*H*-pyrrol-3-amine (4ca)

Following the typical procedure gave the product as a dark red solid; yield: 49 mg (92%).

IR (neat): 3354, 2973, 2928, 1630, 1600, 1568, 1342, 1225, 1089, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.9 Hz, 1 H), 7.69–7.65 (m, 2 H), 7.32 (d, *J* = 8.7 Hz, 3 H), 7.27 (d, *J* = 7.6 Hz, 2 H), 6.14 (s, 1 H), 5.51 (s, 1 H), 2.66 (s, 3 H), 1.44 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.08, 154.35, 145.55, 138.98, 134.43, 131.88, 131.07, 129.70, 128.77, 127.63, 125.77, 93.26, 52.42, 28.70, 22.28.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}ClN_3$: 352.1575; found: 352.1561.

N-*tert*-Butyl-2-[(4-chlorophenyl)imino]-5-(*o*-tolyl)-2*H*-pyrrol-3-amine (4da)

Following the typical procedure gave the product as a purple solid; yield: 50 mg (95%).

IR (neat): 3351, 2974, 2926, 1631, 1596, 1578, 1340, 1227, 1088, 737 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 1 H), 7.89 (d, *J* = 4.3 Hz, 1 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 7.36 (s, 2 H), 7.34 (d, *J* = 2.4 Hz, 2 H), 6.22 (s, 1 H), 5.71 (s, 1 H), 2.43 (s, 3 H), 1.46 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.19, 165.15, 155.27, 145.67, 138.33, 133.89, 133.68, 131.91, 129.42, 128.83, 128.49, 127.89, 126.26, 89.80, 52.44, 28.71, 21.52.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}ClN_3$: 352.1575; found: 352.1559.

N-*tert*-Butyl-2-[(4-chlorophenyl)imino]-5-(4-methoxyphenyl)-2*H*-pyrrol-3-amine (4ea)

Following the typical procedure gave the product as a dark red solid; yield: 48 mg (87%).

IR (neat): 3351, 2974, 2932, 1628, 1594, 1574, 1417, 1352, 1257, 1167 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.9 Hz, 2 H), 7.73 (d, *J* = 8.7 Hz, 2 H), 7.34 (d, *J* = 8.7 Hz, 2 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 6.17 (s, 1 H), 5.68 (s, 1 H), 3.88 (s, 3 H), 1.46 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.05, 165.36, 163.67, 155.10, 145.91, 131.57, 131.20, 128.74, 127.86, 126.54, 114.04, 89.30, 55.60, 52.30, 28.67.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}ClN_3O$: 368.1524; found: 368.1507.

N-*tert*-Butyl-2-[(4-chlorophenyl)imino]-5-[4-(trifluoromethyl)phenyl]-2*H*-pyrrol-3-amine (4fa)

Following the typical procedure gave the product as a dark red solid; yield: 44 mg (72%).

IR (neat): 3349, 2974, 2928, 1617, 1601, 1577, 1417, 1319, 1167, 1089, 841 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.1 Hz, 2 H), 7.76–7.73 (m, 2 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 7.36 (d, *J* = 8.7 Hz, 2 H), 6.36 (s, 1 H), 5.70 (s, 1 H), 1.48 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.46, 156.06, 145.22, 137.38, 133.85, 133.53, 132.44, 128.99, 127.92, 125.49, 122.62, 89.54, 77.48, 77.16, 76.84, 52.79, 28.75.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{20}ClF_3N_3$: 406.1292; found: 406.1276.

4-{3-(*tert*-Butylamino)-2-[(4-chlorophenyl)imino]-2*H*-pyrrol-5-yl}benzonitrile (4ga)

Following the typical procedure gave the product as a dark red solid; yield: 46 mg (85%).

IR (neat): 3348, 2957, 2925, 2228, 1628, 1598, 1569, 1414, 1347, 1283, 1226, 1089, 843 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.3 Hz, 2 H), 7.76 (d, *J* = 1.7 Hz, 1 H), 7.75–7.73 (m, 2 H), 7.72 (s, 1 H), 7.37 (d, *J* = 8.6 Hz, 2 H), 6.41 (s, 1 H), 5.68 (s, 1 H), 1.48 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.08, 156.33, 145.01, 138.17, 132.58, 132.27, 129.03, 127.88, 118.60, 115.29, 89.45, 52.93, 28.76.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{20}ClN_4$: 363.1371; found: 363.1356.

N-*tert*-Butyl-2-[(4-chlorophenyl)imino]-5-(4-fluorophenyl)-2*H*-pyrrol-3-amine (4ha)

Following the typical procedure gave the product as a dark red solid; yield: 45 mg (84%).

IR (neat): 3347, 2975, 2931, 1632, 1591, 1507, 1416, 1228, 1153, 843, 751 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 8.9, 5.6 Hz, 2 H), 7.74–7.70 (m, 2 H), 7.37–7.33 (m, 2 H), 7.19–7.12 (m, 2 H), 6.27 (s, 1 H), 5.67 (s, 1 H), 1.47 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.92, 155.60, 145.58, 132.04, 131.32, 130.28, 128.85, 127.88, 115.93, 115.71, 89.29, 52.53, 28.71.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{20}ClFN_3$: 356.1324; found: 356.1308.

N-*tert*-Butyl-5-(4-chlorophenyl)-2-[(4-chlorophenyl)imino]-2*H*-pyrrol-3-amine (4ia)

Following the typical procedure gave the product as a dark red solid; yield: 50 mg (89%).

IR (neat): 3348, 2973, 2927, 1628, 1605, 1590, 1568, 1408, 1343, 1225, 1089, 1012, 840, 745 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.7 Hz, 2 H), 7.75–7.69 (m, 2 H), 7.46–7.42 (m, 2 H), 7.37–7.33 (m, 2 H), 6.27 (s, 1 H), 5.66 (s, 1 H), 1.46 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.58, 164.79, 155.73, 145.48, 138.85, 132.49, 132.15, 130.22, 128.90, 127.89, 89.31, 52.59, 28.72.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{20}Cl_2N_3$: 372.1029; found: 372.1030.

5-(4-Bromophenyl)-*N*-*tert*-butyl-2-[(4-chlorophenyl)imino]-2*H*-pyrrol-3-amine (4ja)

Following the typical procedure gave the product as a dark red solid; yield: 57 mg (91%).

IR (neat): 3347, 2974, 2930, 1628, 1605, 1566, 1508, 1480, 1404, 1341, 1225, 1088, 1009, 839, 742 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.5 Hz, 2 H), 7.72 (d, *J* = 8.7 Hz, 2 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 6.33 (s, 1 H), 5.65 (s, 1 H), 1.46 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.68, 164.76, 155.73, 145.47, 132.90, 132.14, 131.87, 130.33, 128.85, 127.88, 127.50, 89.25, 52.58, 28.70.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{20}BrClN_3$: 418.0503; found: 418.0484.

5-(Benzo[*b*]thiophen-2-yl)-*N*-*tert*-butyl-2-[(4-chlorophenyl)imino]-2*H*-pyrrol-3-amine (4ka)

Following the typical procedure gave the product as a dark red solid; yield: 41 mg (69%).

IR (neat): 3353, 2975, 2930, 1629, 1601, 1523, 1439, 1365, 1224, 1088, 842, 748 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1 H), 7.87 (t, *J* = 6.3 Hz, 2 H), 7.80–7.76 (m, 2 H), 7.45–7.38 (m, 2 H), 7.38–7.35 (m, 2 H), 6.24 (s, 1 H), 5.70 (d, *J* = 1.8 Hz, 1 H), 1.47 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.42, 155.20, 145.46, 142.70, 139.72, 132.21, 129.09, 128.86, 128.25, 126.93, 125.20, 124.89, 122.89, 89.74, 52.50, 28.68.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}ClN_3S$: 394.1139; found: 394.1123.

4-{[3-(*tert*-Butylamino)-5-phenyl-2*H*-pyrrol-2-ylidene]amino}benzonitrile (4ab)

Following the typical procedure gave the product as a dark red solid; yield: 30 mg (61%).

IR (neat): 3349, 2973, 2930, 2223, 1609, 1508, 1455, 1422, 1355, 1281, 1026, 829 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.1 Hz, 2 H), 7.67 (q, *J* = 8.6 Hz, 4 H), 7.59–7.53 (m, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 6.28 (s, 1 H), 5.74 (s, 1 H), 1.48 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.35, 155.29, 151.18, 133.47, 133.10, 132.57, 129.01, 128.55, 125.93, 119.39, 108.47, 89.76, 52.69, 28.58.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}N_4$: 329.1761; found: 329.1746.

N-*tert*-Butyl-2-[(4-methoxyphenyl)imino]-5-phenyl-2*H*-pyrrol-3-amine (4ac)

Following the typical procedure gave the product as a dark red solid; yield: 47 mg (94%).

IR (neat): 3352, 2975, 2930, 1607, 1508, 1455, 1273, 1109, 728 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.5 Hz, 4 H), 7.68 (s, 2 H), 7.51 (d, *J* = 27.3 Hz, 3 H), 6.29 (s, 1 H), 5.75 (s, 1 H), 3.93 (s, 3 H), 1.49 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.16, 155.42, 151.34, 133.86, 132.93, 130.30, 129.07, 128.64, 127.05, 125.26, 89.93, 52.77, 52.14, 28.78.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{21}H_{23}N_3OK$: 372.1473; found: 372.1456.

N-*tert*-Butyl-2-[(2,6-dimethylphenyl)imino]-5-phenyl-2*H*-pyrrol-3-amine (4ad)

Following the typical procedure gave the product as a dark red solid; yield: 42 mg (85%).

IR (neat): 2963, 2126, 1367, 1239, 1183, 841 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.2 Hz, 2 H), 7.51–7.46 (m, 1 H), 7.43–7.37 (m, 2 H), 7.05 (d, *J* = 7.4 Hz, 2 H), 6.98–6.93 (m, 1 H), 6.14 (s, 1 H), 5.69 (d, *J* = 1.2 Hz, 1 H), 2.14 (s, 6 H), 1.47 (d, *J* = 1.2 Hz, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.48, 165.06, 153.29, 146.73, 134.10, 132.59, 128.95, 128.47, 127.76, 123.98, 120.97, 90.33, 52.33, 28.70, 18.95.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{26}N_3$: 332.2121; found: 332.3112.

(*Z*)-*N*-*tert*-Butyl-5-phenyl-2-[(4-(trifluoromethyl)phenyl)imino]-2*H*-pyrrol-3-amine (4ae)

Following the typical procedure gave the product as a black solid; yield: 31 mg (55%).

IR (neat): 3356, 2975, 2928, 1610, 1510, 1455, 1321, 1118, 853 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.15–8.06 (m, 2 H), 7.67 (dd, *J* = 24.0, 8.5 Hz, 4 H), 7.49 (dt, *J* = 8.5, 7.1 Hz, 3 H), 6.28 (s, 1 H), 5.74 (s, 1 H), 1.48 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.78 (s), 166.22 (s), 155.39 (s), 150.32 (s), 133.90 (s), 132.98 (s), 129.11 (s), 128.66 (s), 125.76 (dd, *J* = 9.3, 5.4 Hz), 89.98 (s), 52.73 (s), 28.78 (s).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}F_3N_3$: 372.1682; found: 372.1673.

(*Z*)-*N*-*tert*-Butyl-2-[(4-nitrophenyl)imino]-5-phenyl-2*H*-pyrrol-3-amine (4af)

Following the typical procedure gave the product as a black solid; yield: 26 mg (50%).

IR (neat): 3348, 2925, 2853, 1609, 1509, 1455, 1337, 1025, 864 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 9.0 Hz, 2 H), 8.10 (dd, 2 H), 7.68 (d, *J* = 9.0 Hz, 2 H), 7.57 (s, 1 H), 7.53–7.45 (m, 2 H), 5.75 (s, 1 H), 1.49 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.69 (s), 166.78 (s), 155.55 (s), 153.38 (s), 145.07 (s), 133.65 (s), 133.33 (s), 129.23 (s), 128.74 (s), 125.64 (s), 124.39 (s), 90.05 (s), 52.98 (s), 28.79 (s).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}N_4O_2$: 349.1659; found: 349.1650.

N-*tert*-Butyl-2-(cyclohexylimino)-5-phenyl-2*H*-pyrrol-3-amine (4ag)

Following the typical procedure gave the product as a dark red solid; yield: 9 mg (21%).

IR (neat): 3232, 2930, 2855, 1685, 1597, 1453, 1328, 1060, 728 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.84 (m, 2 H), 7.59 (m, 3 H), 6.03 (s, 1 H), 3.93 (m, 1 H), 1.95 (m, 2 H), 1.78–1.62 (m, 4 H), 1.53 (s, 9 H), 1.45-1.26 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.96, 159.84, 153.15, 133.71, 129.73, 127.68, 127.48, 94.38, 77.48, 77.16, 76.84, 58.97, 58.73, 33.52, 30.47, 24.98, 24.68.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{28}N_3$: 310.2278; found: 310.2265.

2-(*tert*-Butylimino)-*N*-(2,6-dimethylphenyl)-5-phenyl-2*H*-pyrrol-3-amine (4ai)

Following the typical procedure gave the product as a dark red solid; yield: 8 mg (16%).

IR (neat): 2963, 2126, 1367, 1239, 1184, 841 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 6.7, 1.6 Hz, 2 H), 7.38 (d, *J* = 6.4 Hz, 3 H), 7.06 (d, *J* = 7.4 Hz, 2 H), 6.99–6.95 (m, 1 H), 5.38 (d, *J* = 1.1 Hz, 1 H), 2.07 (s, 6 H), 1.62 (d, *J* = 0.9 Hz, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.52 (s), 160.30 (s), 133.22 (s), 129.98 (s), 128.10 (s), 127.44 (s), 126.97 (d, *J* = 6.1 Hz), 125.82 (s), 122.99 (s), 90.89 (s), 51.86 (s), 27.93 (s), 17.45 (s).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{26}N_3$: 332.2121; found: 332.3112.

2-[(4-Chlorophenyl)imino)]-*N*-cyclohexyl-5-phenyl-2*H*-pyrrol-3-amine (4ak)

Following the typical procedure gave the product as a dark red solid; yield: 51 mg (94%).

IR (neat): 3364, 2930, 2854, 1735, 1609, 1595, 1481, 1356, 1227, 1089, 1011, 842, 725 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.3 Hz, 2 H), 7.76 (d, *J* = 8.5 Hz, 2 H), 7.55–7.42 (m, 3 H), 7.37–7.33 (m, 2 H), 5.69 (s, 1 H), 3.43–3.32 (m, 1 H), 2.07 (s, 2 H), 1.83 (dd, *J* = 8.3, 4.0 Hz, 2 H), 1.69 (d, *J* = 12.3 Hz, 1 H), 1.40 (t, *J* = 9.8 Hz, 5 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.90, 163.84, 158.58, 144.87, 133.96, 132.55, 131.63, 128.86, 128.72, 127.20, 88.80, 55.49, 32.76, 25.64, 24.84.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{23}ClN_3$: 364.1575; found: 364.1560.

N-Cyclohexyl-2-[(2,6-dimethylphenyl)imino]-5-phenyl-2*H*-pyrrol-3-amine (4al)

Following the typical procedure gave the product as a dark red solid; yield: 19 mg (35%).

IR (neat): 3371, 2928, 2853, 1614, 1509, 1455, 1358, 1292, 1015, 727 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.2 Hz, 2 H), 7.48 (d, *J* = 7.4 Hz, 1 H), 7.40 (t, *J* = 7.5 Hz, 2 H), 7.05 (d, *J* = 7.4 Hz, 2 H), 6.97 (d, *J* = 6.8 Hz, 1 H), 5.63 (s, 1 H), 3.36 (s, 1 H), 2.14 (s, 6 H), 1.74 (dd, *J* = 41.9, 19.6 Hz, 5 H), 1.43 (t, *J* = 8.8 Hz, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.96, 155.74, 152.64, 146.45, 133.92, 133.03, 132.36, 128.49, 128.34, 127.69, 127.60, 127.01, 89.27, 54.29, 32.44, 29.68, 25.53, 24.66, 18.74.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{28}N_3$: 358.2278; found: 358.2263.

N-Butyl-2-[(4-chlorophenyl)imino]-5-phenyl-2*H*-pyrrol-3-amine (4am)

Following the typical procedure gave the product as a dark red solid; yield: 46 mg (90%).

IR (neat): 3350, 2959, 2931, 1635, 1596, 1558, 1492, 1404, 1314, 1091, 829, 753 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.14–8.08 (m, 2 H), 7.79–7.73 (m, 2 H), 7.52 (d, *J* = 7.2 Hz, 1 H), 7.47 (dd, *J* = 8.1, 6.5 Hz, 2 H), 7.37–7.34 (m, 2 H), 6.04 (s, 1 H), 5.70 (s, 1 H), 3.37 (t, *J* = 7.1 Hz, 2 H), 1.72 (dt, *J* = 19.9, 7.4 Hz, 2 H), 1.47 (dt, *J* = 15.0, 7.4 Hz, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.95, 132.60, 128.79, 127.24 (s), 122.89, 88.93, 46.41, 31.41, 20.41, 13.95.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}ClN_3$: 338.1419; found: 338.1400.

2-[(4-Chlorophenyl)imino]-*N*-(4-methoxyphenyl)-5-phenyl-2*H*-pyrrol-3-amine (4an)

Following the typical procedure gave the product as a dark red solid; yield: 29 mg (50%).

IR (neat): 3350, 2948, 1715, 1595, 1456, 1278, 841, 768 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 7.1 Hz, 2 H), 8.09 (d, *J* = 8.5 Hz, 2 H), 7.85 (d, *J* = 8.7 Hz, 2 H), 7.56 (d, *J* = 7.1 Hz, 1 H), 7.50 (dd, *J* = 10.0, 4.8 Hz, 2 H), 7.43–7.37 (m, 2 H), 7.28–7.22 (m, 2 H), 6.38 (s, 1 H), 3.93 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.64, 133.21, 132.42, 131.41, 130.94, 129.61, 129.29–128.67, 128.40, 126.76, 125.12, 122.85, 118.41, 95.39, 52.23.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{19}ClN_3O$: 388.1211; found: 388.1372.

2-[(4-Chlorophenyl)imino]-*N*-(4-cyanophenyl)-5-phenyl-2*H*-pyrrol-3-amine (4ao)

Following the typical procedure gave the product as a dark red solid; yield: 30 mg (52%).

IR (neat): 3319, 2925, 2222, 1594, 1530, 1456, 1351, 1089, 828 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.11 (m, 2 H), 8.05 (s, 1 H), 7.86 (d, *J* = 8.7 Hz, 2 H), 7.70 (d, *J* = 8.6 Hz, 2 H), 7.52 (t, *J* = 7.5 Hz, 2 H), 7.43–7.38 (m, 2 H), 7.31–7.25 (m, 3 H), 6.38 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 133.84, 133.23, 132.52, 129.95, 129.47, 129.23, 128.98, 126.69, 126.17, 122.79, 122.19, 119.06, 95.85.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{16}ClN_4$: 383.1058; found: 383.1041.

2-[(4-Chlorophenyl)imino]-*N*-(2,6-dimethylphenyl)-5-phenyl-2*H*-pyrrol-3-amine (4ap)

Following the typical procedure gave the product as a dark red solid; yield: 37 mg (64%).

IR (neat): 3352, 2975, 1607, 1508, 1455, 1273, 1109, 728 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 6.4 Hz, 2 H), 7.95 (d, *J* = 8.8 Hz, 2 H), 7.45 (dd, *J* = 9.1, 6.1 Hz, 3 H), 7.42–7.39 (m, 2 H), 7.10 (t, *J* = 9.6 Hz, 3 H), 5.53 (s, 1 H), 2.42 (s, 1 H), 2.15 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.32, 133.34, 131.67, 129.68, 129.12, 128.53, 128.38, 127.61, 125.07, 122.40, 92.74, 18.36.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{21}ClN_3$: 386.1419; found: 386.1403.

_N_-(2,6-Dimethylphenyl)-2-[(2,6-dimethylphenyl)imino]-5-phenyl-2_H_-pyrrol-3-amine (4aq)[4]

Following the typical procedure gave the product as a dark red solid; yield: 47 mg (83%).

IR (neat): 3352, 2975, 1607, 1508, 1455, 1273, 1109, 728 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.5 Hz, 1 H), 7.40 (d, *J* = 2.2 Hz, 3 H), 7.15–7.05 (m, 7 H), 6.99 (dd, *J* = 12.6, 7.5 Hz, 3 H), 6.41 (s, 1 H), 5.47 (s, 1 H), 2.24 (s, 6 H), 2.17 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.72, 155.85, 149.86, 146.10, 131.74, 129.17, 128.54, 128.33, 127.85, 127.59, 126.56, 125.97, 123.81, 123.44, 94.85, 18.21.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{26}N_3$: 380.2121; found: 380.2112.

Funding Information

This project is supported by the Inner Mongolia University (Enhancing Comprehensive Strength Foundation, Grant No. 10000-1601010981), and National Natural Science Foundation of China (Grants No. 21672256 and 21562032).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611830.

References

(1) For examples, see: (a) Furstner, A. *Angew. Chem. Int. Ed.* **2003**, *42*, 3582. (b) Parikh, S. A.; Kantarjian, H.; Schimmer, A.; Walsh, W.; Asatiani, E.; El-Shami, K.; Winton, E.; Verstovsek, S. *Clin. Lymphoma Myeloma* **2010**, *10*, 285. (c) Hernández, P. I.; Moreno, D.; Javier, A. A.; Torroba, T.; Pérez-Tomás, R.; Quesada, R. *Chem. Commun.* **2012**, *48*, 1556.

(2) For examples, see: (a) Gorman, A.; Killoran, J.; O'Shea, C.; Kenna, T.; Gallagher, W. M.; O'Shea, D. F. *J. Am. Chem. Soc.* **2004**, *126*, 10619. (b) Coskun, A.; Yilmaz, M. D.; Akkaya, E. U. *Org. Lett.* **2007**, *9*, 607. (c) Amin, A. N.; El-Khouly, M. E.; Subbaiyan, N. K.; Zandler, M. E.; Fukuzumi, S.; D'Souza, F. *Chem. Commun.* **2012**, *48*, 206. (d) Liu, S.; Shi, Z.; Xu, W.; Yang, H.; Xi, N.; Liu, X.; Zhao, Q.; Huang, W. *Dyes Pigm.* **2014**, *103*, 145.

(3) Hu, W.; Li, J.; Xu, Y.; Li, J.; Wu, W.; Liu, H.; Jiang, H. *Org. Lett.* **2017**, *19*, 678.

(4) Senadi, G. C.; Lu, T.-Y.; Dhandabani, G. K.; Wang, J.-J. *Org. Lett.* **2017**, *19*, 1172.

(5) Capuano, L.; Dahm, B.; Port, V.; Schnur, R.; Schramm, V. *Chem. Ber.* **1988**, *121*, 271.

(6) For selected reviews, see: (a) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem. Int. Ed.* **2005**, *44*, 5188. (b) Bräse, S.; Banert, K. *Organic Azides: Syntheses and Applications*; Wiley-VCH: Weinheim, **2010**. (c) Driver, T. G. *Org. Biomol. Chem.* **2010**, *8*, 3831. (d) Intrieri, D.; Zardi, P.; Caselli, A.; Gallo, E. *Chem. Commun.* **2014**, *50*, 11440. (e) Shin, K.; Kim, H.; Chang, S. *Acc. Chem. Res.* **2015**, *48*, 1040.

(7) (a) Cowley, R. E.; Golder, M. R.; Eckert, N. A.; Al-Afyouni, M. H.; Holland, P. L. *Organometallics* **2013**, *32*, 5289. (b) Wiese, S.; Aguila, M. J. B.; Kogut, E.; Warren, T. H. *Organometallics* **2013**, *32*, 2300. (c) Zhang, Z.; Li, Z.; Fu, B.; Zhang, Z. *Chem. Commun.* **2015**, *51*, 16312. (d) Zhang, Z.; Xiao, F.; Huang, B.; Hu, J.; Fu, B.; Zhang, Z. *Org. Lett.* **2016**, *18*, 908. (e) Chen, K.; Tang, X. Y.; Shi, M. *Chem. Commun.* **2016**, *52*, 1967. (f) Zhang, Z.; Huang, B.; Qiao, G.; Zhu, L.; Xiao, F.; Chen, F.; Bin, F.; Zhang, Z. *Angew. Chem. Int. Ed.* **2017**, *56*, 4320. (g) Gu, Z.; Liu, Y.; Wang, F.; Bao, X.; Wang, S.; Ji, S. *ACS Catal.* **2017**, *7*, 3893. (h) Li, Z.; Huo, T.; Li, L.; Feng, S.; Wang, Q.; Zhang, Z.; Pang, S.; Zhang, Z.; Wang, P.; Zhang, Z. *Org. Lett.* **2018**, *20*, 7762. (i) He, Y.; Yuan, C.; Shuai, L.; Xiao, Q. *Org. Lett.* **2019**, *21*, 185.