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FULL PAPER

Polyoxometalate immobilized on MOF-5 as an environment-friendly catalyst for the synthesis of poly-functionalized 3-pyrrolin-2-ones

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A polyoxometalate immobilized on MOF-5 (POM/MOF-5) material has been synthesized and evaluated for the diversity-oriented synthesis of poly-functionalized 3-pyrrolin-2-ones via pseudo-four-component reaction between dialkyl acetylenedicarboxylate, amines, and aldehyde. The catalyst can be separated from the reaction mixture and reused at least five times with superior activity.

KEYWORDS
3-pyrrolin-2-ones, heterogeneous catalyst, MOF-5, multicomponent reaction, polyoxometalate

1 | INTRODUCTION

Polyoxometalates (POM) are well-known catalysts because of their unique redox properties, tunable acidity, and possibility of the catalyst design at atomic/molecular levels, which have been employed rather extensively as catalysts for various organic reactions over the past few decades, including oxidation,[1] reduction,[2] multicomponent,[3] esterification and transesterification,[4] and C–C coupling[5] reactions. They could be designed as multifunctional catalysts, based on different metal atoms or heteroatoms in their structure, counter cations, second structures.[6] However, the inherent shortcomings of their high solubility, low surface area, and instability under reaction conditions impeded the further application of POM-based catalysts. Metal–organic frameworks (MOFs) as a promising catalyst support have drawn significant attention because of their large specific surface areas, tunable pore distributions, abundant aromatic ligands, outstanding thermal and solvent stabilities, high acid–base catalytic activities, and ease of functionalization and design.[7] Recently, polyoxometalates/metal–organic frameworks (POM/MOFs) materials have been reported for several applications including proton conduction,[8] gas storage/separation,[9] drug carriers,[10] solid electrolytes,[11] photosensitizers,[12] and catalysis.[13] Combining the high catalytic activity of particular POM with the large surface area and stability of MOF to develop a new efficient and environmentally friendly catalyst for catalytic organic transformations is therefore an interesting challenge.

Nitrogen-containing heterocycles are an important structural unit and play an essential role in natural, pharmaceutical, and coordination chemistry.[14] In particular, pyrrole and pyrrolidine derivatives as five-membered nitrogen-containing heterocycles are common core scaffolds in natural products and pharmaceutical agents.[15]

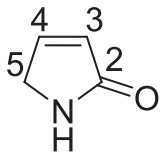
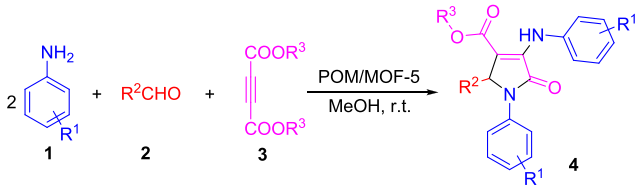


FIGURE 1 3-Pyrrolin-2-one

The 3-pyrrolin-2-one moiety (Figure 1) is a structural component found in a large number of natural products including spongolactams,[16] oteromycin,[17] echinophyllins,[18] and salipyrrolidinone A.[19] Moreover, 3-pyrrolin-2-ones that contain the γ-lactam ring have proven to be useful scaffolds in the discovery of novel drug entities, such as COX-II inhibitors,[20] VEGF-R inhibitors,[21] HIV-1 integrase inhibitors,[22] HDAC inhibitors,[23] antitumor agents,[24] neurological agents,[25] and novel G0/G1-phase arresting agents.[26] Furthermore, the ring conjugate system of these functionalized lactams favors its potential as intermediates in synthetic chemistry.[27] Therefore, synthetic interest in 3-pyrrolin-2-ones arises from their occurrence in nature, diverse biological activity, and utility as building blocks for the preparation of nitrogen heterocycles and γ-amino acid derivatives.[28]

Among the many synthetic approaches to *N*-heterocycles, multicomponent coupling reaction that is a powerful synthetic tool to provide structurally complex molecules in a single pot has become increasingly attractive.[29] Recently, a few protocols for synthesis poly-functionalized 3-pyrrolin-2-ones via the four-component reaction of dialkyl acetylenedicarboxylate, aldehyde, and amines in the presence of lemon juice,[30] UiO-66-SO_3H,[31] Cu $(OAc)_2{\cdot}H_2O$,[32] perovskite-structured $BiFeO_3$ nanoparticles,[33] molecular iodine,[34] TiO_2 nanopowder,[35] or BF_3/nano-sawdust[36] have been developed. In continuation of our effort to develop efficient and reusable heterogeneous catalysts for green synthetic methods,[37] herein, we report on the preparation of a POM/MOF-5 and its application as a heterogeneous catalyst for the synthesis of poly-functionalized 3-pyrrolin-2-ones (Scheme 1).



SCHEME 1 POM/MOF-5-catalyzed four-component reaction of dialkyl acetylenedicarboxylate, aldehyde, and amines

2 | RESULTS AND DISCUSSION

2.1 | Preparation and characterization of POM/MOF-5 catalyst

POM/MOF-5 composite catalyst was prepared by heating $H_3PMo_{12}O_{40}$, zinc nitrate, 1,4-benzenedicarboxylic acid (H_2BDC), and $(CH_3)_4NOH$ at 180°C for 24 h, which were fully characterized by Fourier-transform infrared spectroscopy (FTIR) spectra, powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and SEM energy dispersive X-ray spectroscopy (EDS), and thermogram (TG).

The FTIR spectrum of pure H_2BDC, $H_3PMo_{12}O_4$, MOF, and POM/MOF-5 is displayed in Figure 2. The spectra of POM/MOF-5 contain not only typical infrared bands belonging to MOF-5 but also Mo–O bands appertaining to POM. The spectra of POM/MOF-5 displayed absorption peaks at 1062, 959, 879, and 802 cm^{-1} corresponding to the P═O, Mo═O, Mo–O_b–Mo, and Mo–O_c–Mo band vibration of $H_3PMo_{12}O_{40}$, respectively.[38] The characteristic peaks related to MOF-5 and $H_3PMo_{12}O_4$ particles are slightly shifted. These shifts indicate that a strong interaction exists between the POM anion and MOF-5.

The XRD patterns of POM, MOF-5, and POM/POM are provided in Figure 3. Upon immobilizing of POM on MOF-5, the main peaks contributed to POM and MOF-5 are observed, whereas the intensities of the peaks at low angles decrease. These findings suggest the encapsulation of POM in the cavities of MOF-5 and the intact of the ordered structure of MOF-5.

As shown in Figure 4, the SEM of POM/MOF-5 catalyst demonstrates that the particles are highly crystalline

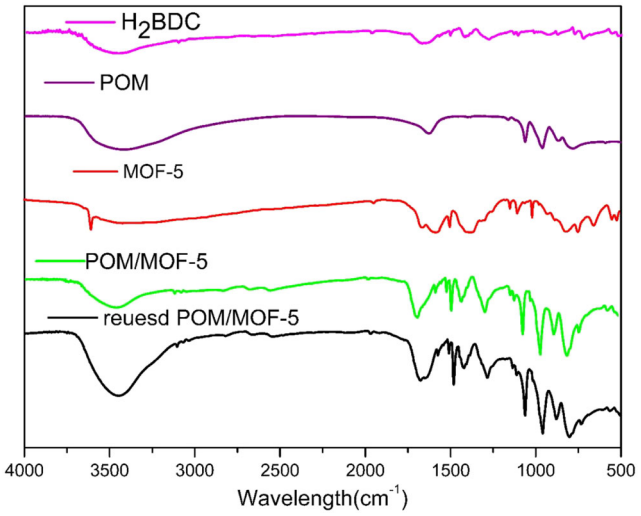


FIGURE 2 FTIR spectra of H_2DBC, $H_3PMo_{12}O_{40}$, MOF-5, and POM/MOF-5

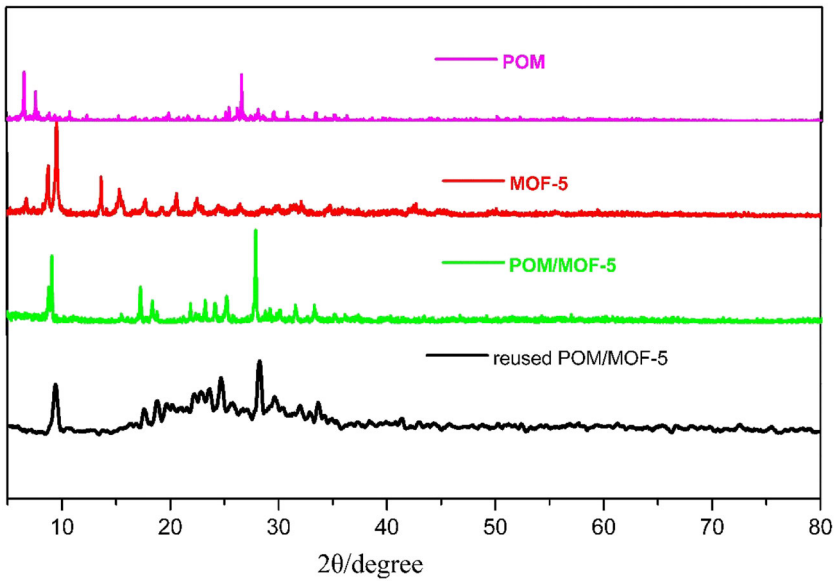


FIGURE 3 XRD pattern of $H_3PMo_{12}O_{40}$, MOF-5, and POM/MOF-5

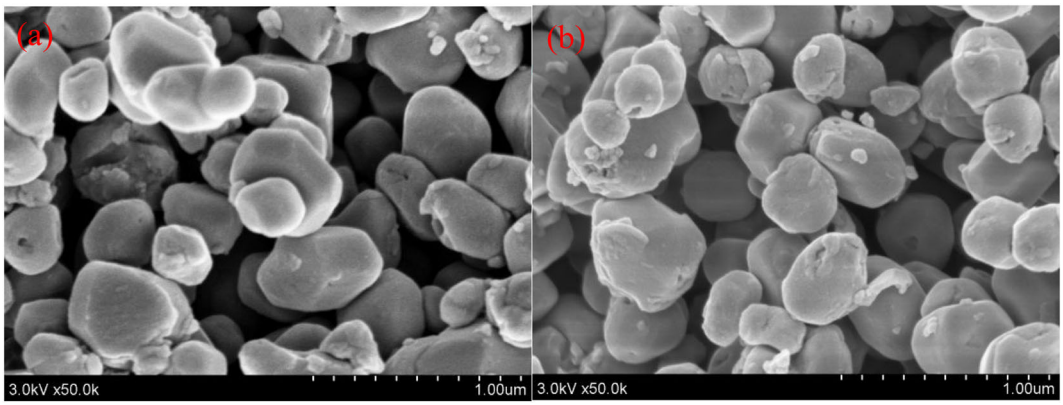


FIGURE 4 SEM image of POM/MOF-5

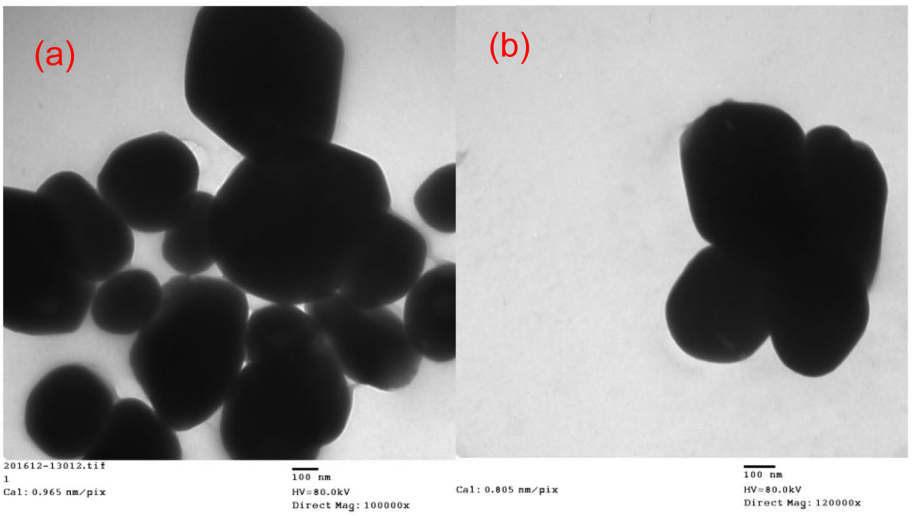


FIGURE 5 TEM image of POM/MOF-5

cubic structure, which was also in a good agreement with the results from TEM (Figure 5). TEM and SEM images collected demonstrate that POM encapsulation is limited. EDS analysis indicates the presence of elements C, O, Zn, P, and Mo (Figure 6). The presence of Mo confirms the loading of PMo_{12} onto the MOF-5 surface or into the

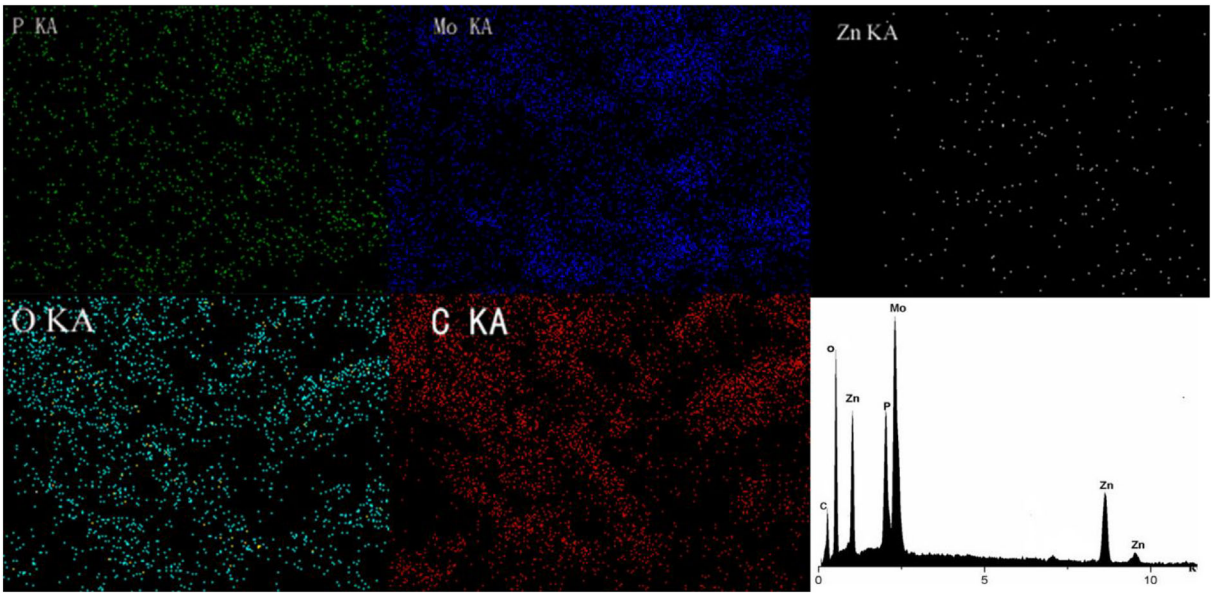


FIGURE 6 EDX mapping image of POM/MOF-5

pores. Furthermore, element mapping was adopted in order to further describe the spatial distribution and the combination of MOF-5 and $H_3PMo_{12}O_4$. The data revealed the presence and homogeneous distribution of POM clusters in these materials. The nitrogen absorption–desorption measurements indicate that POM/MOF-5 had a specific surface area of 165 m^2g^{-1} (Figure 7).

POM/MOF-5 has good thermal stability, as can be learned from the TG shown in Figure 8. TGA experiments were carried out under an air atmosphere from 20°C to 800°C. The weight loss below 300°C resulted from the occluded $(CH_3)_4N^+$ and water. POM/MOF-5 began to decompose above 450°C, which is much higher than the reaction temperatures of the synthesis reaction.

2.2 | Optimization of reaction conditions

The activity of the prepared catalyst was tested for the reaction of aniline (2.0 mmol), benzaldehyde (1.0 mmol), and dimethyl but-2-ynedioate (1.0 mmol) at room temperature. The reaction, as shown in Table 1, proceeded very slowly in the absence of catalyst, and only a trace of desired product **4a** was found after heating for 6 h (Table 1, entry 1). Different heterogeneous catalysts such as Fe-MIL-101, UiO-66, Cu-BTC, IRMOF-3, MIL-53(Al), and MOF-5 on the reaction were investigated and gave the desired product **4a** in 25%–43% yields (Table 1, entries 2–7). Pleasingly, when POM (Mo)/MOF-5 was used as the catalyst, the reaction yield can be significantly improved (91%; Table 1, entry 9). It was noted that when the reaction was performed in the same conditions in

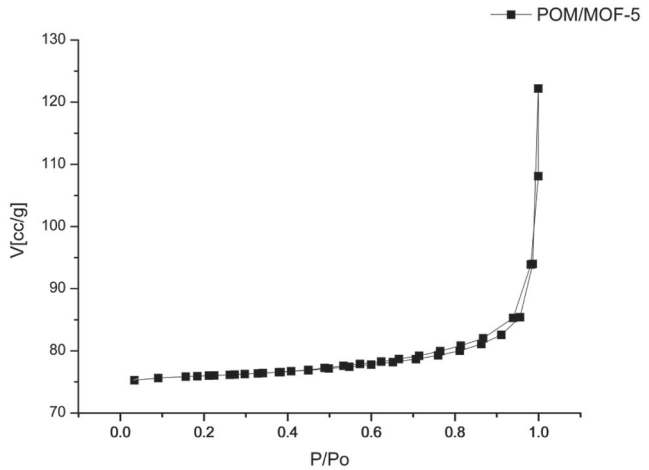


FIGURE 7 Nitrogen adsorption and desorption curves of POM/MOF-5

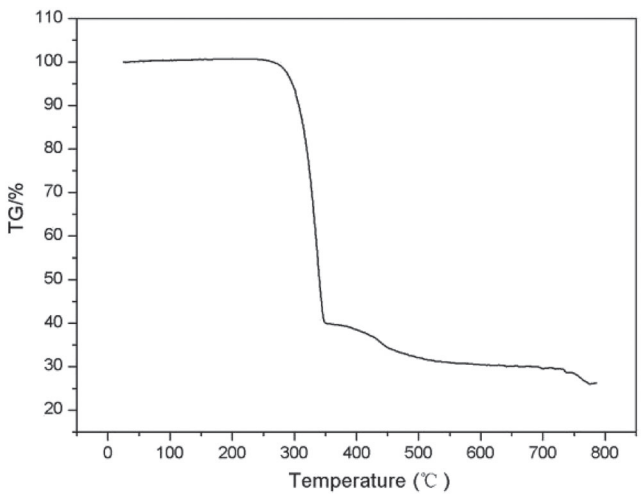
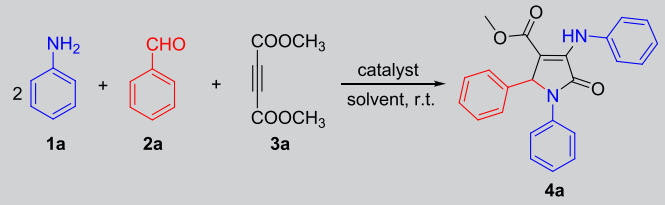


FIGURE 8 Thermogram of POM/MOF-5

TABLE 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]
1	no	MeOH	6.0	trace
2	Fe-MIL-101	MeOH	3.0	25
3	UiO-66	MeOH	3.0	32
4	Cu-BTC	MeOH	3.0	35
5	IRMOF-3	MeOH	3.0	29
6	MIL-53(Al)	MeOH	3.0	30
7	MOF-5	MeOH	3.0	43
8	POM(W)/MOF-5	MeOH	3.0	61
9	POM (Mo)/MOF-5	MeOH	3.0	91
10	POM (Mo)/MOF-5	EtOH	3.0	85
11	POM (Mo)/MOF-5	DMF	3.0	10
12	POM (Mo)/MOF-5	CH_3CN	3.0	52
13	POM (Mo)/MOF-5	THF	3.0	25
14	POM (Mo)/MOF-5	*n*-hexane	3.0	62
15	POM (Mo)/MOF-5	CH_2Cl_2	3.0	42
16[c]	POM (Mo)/MOF-5	MeOH	3.0	41
17[d]	POM (Mo)/MOF-5	MeOH	3.0	70
18[e]	POM (Mo)/MOF-5	MeOH	3.0	91
19[f]	POM (Mo)/MOF-5	MeOH	3.0	92

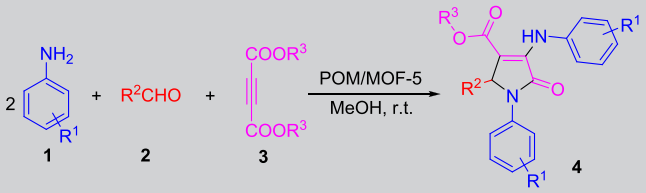
[a]Reaction conditions: **1a** (2.0 mmol), **2a** (1.0 mmol), **3a** (1.0 mmol), and 10-mg catalyst in the solvent (2.0 mL) at room temperature for 3 h.
[b]Isolated yields.
[c]3-mg catalyst was used.
[d]5-mg catalyst was used.
[e]15-mg catalyst was used.
[f]50-mmol scale.

entry 8 with POM(W)/MOF-5, desired product was obtained in low yield. Investigation of the effect of solvents such as methanol, ethanol, *N*,*N*-dimethylformamide (DMF), acetonitrile, tetrahydrofuran, *n*-hexane, and dichloromethane showed that methanol gave the best result for this transformation, affording the product **4a** in 91% yield (Table 1, entries 9–15). The yield was greatly affected by the amount of catalyst. When 3.0 and 5.0 mg of the catalyst was used, the yields were 41% and 70%, respectively (Table 1, entries 16 and 17). And increasing the catalyst amount to 15 mg did not produce better results (Table 1, entry 18). To demonstrate preparative utility, we also enlarged the reaction scale to 50 mmol for the model reaction, and it was found that the reaction yield reached the same level as when it was performed on a small scale (Table 1, entry 19). Therefore, the optimal reaction conditions were determined to be the following: 10 mg POM (Mo)/MOF-5 in 2 ml MeOH at room temperature for 3 h.

2.3 | Synthesis of poly-functionalized 3-pyrrolin-2-ones

Having the optimal conditions in hand, we investigated the substrate scope of this reaction. As shown in Table 2,

TABLE 2 Substrate scope examination[a]



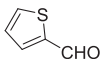
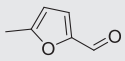
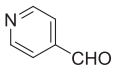
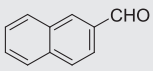
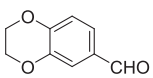
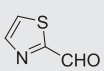
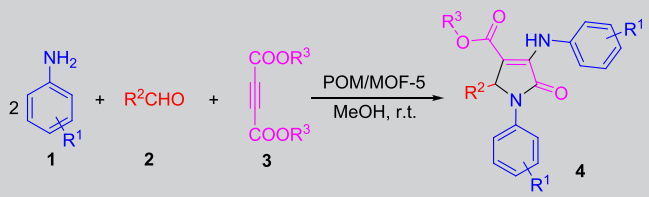
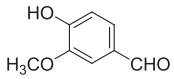
Entry	R^1	Aldehyde	R^3	Product	Time (h)	Yield (%)[b]	m.p. (°C)
1	H	PhCHO	Me	**4a**	2.0	91	177–179 (178–180)[30]
2	H	4-$OCH_3C_6H_4CHO$	Me	**4b**	2.0	86	180–182 (178–180)[33]
3	H	4-$OEtC_6H_4CHO$	Me	**4c**	2.5	87	157–158
4	H	4-C $(CH_3)_3C_6H_4CHO$	Me	**4d**	2.5	89	166–168
5	H	4-OHC_6H_4CHO	Me	**4e**	2.0	82	194–196
6	H	3-FC_6H_4CHO	Me	**4f**	1.5	88	154–156
7	H	2-ClC_6H_4CHO	Me	**4g**	3.0	87	144–146
8	H	3-ClC_6H_4CHO	Me	**4h**	2.5	89	179–181
9	H	4-ClC_6H_4CHO	Me	**4i**	2.5	93	183–184 (168–170)[35]
10	H	3-$CF_3C_6H_4CHO$	Me	**4j**	2.5	90	166–167
11	H	4-$NO_2C_6H_4CHO$	Me	**4k**	2.5	90	156–158 (176–177)[32]
12	H	4-CNC_6H_4CHO	Me	**4l**	3.0	90	178–180
13	H		Me	**4m**	3.5	85	160–162
14	H		Me	**4n**	3.5	86	158–160
15	H		Me	**4o**	4.0	84	200–202
16	H		Me	**4p**	5.0	83	190–192
17	H		Me	**4q**	5.0	81	172–174
18	H		Me	**4r**	4.5	84	138–139

TABLE 2 (Continued)

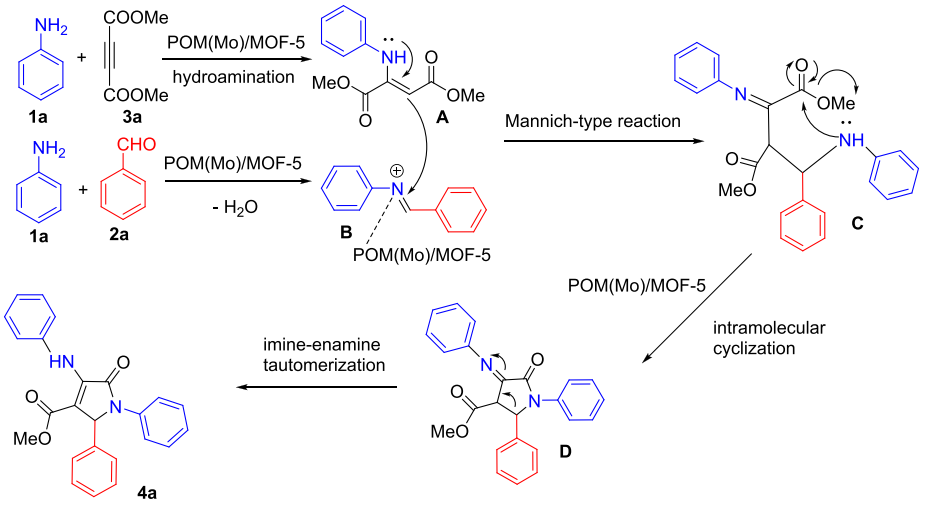


Entry	R^1	Aldehyde	R^3	Product	Time (h)	Yield (%)[b]	m.p. (°C)
19	H		Me	**4s**	4.0	80	192–193 (183–184)[32]
20	4-CH_3	PhCHO	Me	**4t**	3.5	87	181–182 (182–184)[30]
21	4-OCH_3	PhCHO	Me	**4u**	3.5	86	159–161 (170–172)[30]
22	4-F	PhCHO	Me	**4v**	2.5	89	126–128 (133–134)[32]
23	3-Cl	PhCHO	Me	**4w**	2.5	86	139–140
24	3-Br	PhCHO	Me	**4x**	3.0	90	157–159
25	4-Br	PhCHO	Me	**4y**	2.5	88	205–207 (203–205)[30]
26	4-CH_3	4-$CH_3C_6H_4CHO$	Me	**4z**	3.5	86	183–185
27	4-Br	4-$CH_3C_6H_4CHO$	Me	**4aa**	3.0	91	130–132
28	4-CH_3	4-BrC_6H_4CHO	Me	**4ab**	3.0	89	174–175 (146–148)[35]
29	4-Br	4-ClC_6H_4CHO	Me	**4ac**	2.5	92	222–223
30	H	PhCHO	Et	**4ad**	3.0	90	130–131 (110–112)[30]
31	H	3-$OCH_3C_6H_4CHO$	Et	**4ae**	3.0	85	127–129 (107–108)[26]
32	H	3-BrC_6H_4CHO	Et	**4af**	2.5	91	175–176
33	4-Br	PhCHO	Et	**4ag**	2.5	92	151–153

[a]Reaction conditions: **1** (2.0 mmol), **2** (1.0 mmol), **3** (1.0 mmol), and 10-mg POM (Mo)/MOF-5 in 2.0-mL MeOH at room temperature for 1.5-5.0 h.
[b]Isolated yields.

we first examined the reaction of anilines and dimethyl but-2-ynedioate with a diverse array of aldehydes. All of aldehydes with electron-donating or electron-withdrawing substituents were found to be applicable to this reaction and gave the expected products **4a**–**4s** in high to excellent yields. Remarkably, strongly electron-poor aromatic aldehydes such as 4-(trifluoromethyl)benzaldehyde, 4-nitrobenzaldehyde, and 4-formylbenzonitrile afforded the desired products **4j**–**4l** in good yields. The position of substituents has no obvious effect (entries 7–9). Moreover, heterocycle substituted aldehydes such as 2-thenaldehyde, 5-methylfuran-2-carbaldehyde, 4-pyridinecarboxaldehyde, and 1,3-thiazole-2-carbaldehyde were also compatible in this reaction, giving the desired products **4m**–**4o** and **4r** in high yields. 2-Naphthaldehyde and 1,4-benzodioxan-6-carboxaldehyde were also suitable partners and gave the desired products **4p** and **4q** in 83% and 81%, respectively. It is worth noting that disubstituted benzaldehyde such as vanillin was also tolerated and gave the corresponding product **4s** in good yield. Next, a variety of substituted anilines, such as *para* substituents (F, Br, OMe, and CH_3) and *meta* substituents (Cl and Br) were examined. Electron-withdrawing and electron-donating substituents were generally well tolerated, affording the desired products **4t**–**4y** in good yields. Stimulated by these results, the reactions of substituted aromatic aldehydes or substituted anilines were tested under the above optimal conditions, giving the products **4z**–**4ac** in 86%–92% yields. When the corresponding reactions of DEAD were evaluated, similar results were obtained, as expected (entries 30–33).

Based on our findings and previous studies,[33] a possible reaction mechanism for this



SCHEME 2 Plausible reaction mechanism for the synthesis of **4a**

pseudo-four-component reaction is proposed. As shown in Scheme 2, DMAD reacts with the first molecule of aniline in the presence of POM (Mo)/MOF-5 through the 1,4-addition reaction to lead to the formation of hydroamination intermediate **A**. Simultaneously, an imine **B** is produced through the condensation reaction of the second molecule of aniline with the activated benzaldehyde. During the reaction, POM (Mo)/MOF-5 acts as a Lewis acid, accepting a lone pair of electrons from the nitrogen atom of the imine (**B**), resulting in activation of the imine. POM (Mo)/MOF-5 is a more efficient catalyst than POM(W)/MOF-5 in this reaction because of more active Lewis acid properties. This activated imine **B** attacks on intermediate **A** through Mannich-type reaction, leading to the formation of an intermediate **C**. The intermediate **C** undergoes intramolecular cyclization under the catalysis of POM (Mo)/MOF-5 to obtain intermediate **D**, followed by tautomerism to generate final product **4a**.

2.4 | Recyclability of the catalyst

As shown in Figure 9, reusability of the catalyst is examined over POM (Mo)/MOF-5 with the model reaction of anilines, benzaldehyde, and dimethyl but-2-ynedioate, which exhibited the consistent activity for the five consecutive cycles. In this procedure, the catalyst was separated from the reaction mixture by simple filtration. The recovered catalyst was washed with ethyl acetate, dried under vacuum, and then reused directly in model reaction for the next round without further purification. The catalyst can be reused at least five times with essentially no loss of catalytic activity, which indicates that the prepared catalyst possessed excellent activity and reusability.

After the sixth cycle, the reused catalyst was analyzed by XRD, and the results showed that the catalyst fully maintained its structural integrity (Figure 3). FTIR analysis confirms the chemical integrity of the catalyst by comparing it with fresh catalyst (Figure 2). In order to confirm the morphological stability of the catalyst, SEM (Figure 4b) and TEM (Figure 5b) analyses were also performed. The leaching amount of Mo and Zn was also determined by inductively coupled plasma technology. It was found that after the sixth cycle, the content of Mo and Zn in methanol were 0.80 and 0.60 ppm, respectively. These results indicate that the catalyst has excellent stability and durability and can be used multiple times in catalytic conversion.

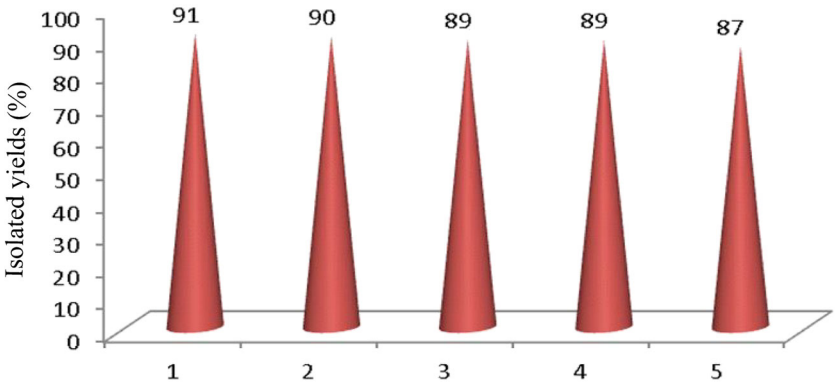


FIGURE 9 Recycling of the catalyst

3 | CONCLUSION

In summary, we have developed a novel and efficient protocol for one-pot synthesis of poly-functionalized 3-pyrrolin-2-ones using the recoverable POM/MOF-5 as catalyst under mild condition. A variety of anilines and various substituted aldehydes can be tolerated, giving the structural diversity of poly-functionalized 3-pyrrolin-2-ones in good to excellent yields. Moreover, the easy recovery and reuse of the catalyst, short reaction time, and ease of product separation make this solution practical, environmentally friendly, and economically attractive.

4 | EXPERIMENTAL

4.1 | Instruments and reagents

All chemicals and solvents were commercially available from Merck, Aldrich, or Fluka as received and used without further purification. X-ray diffraction analysis was carried out using a D8 Advance diffractometer (Bruker AXS, Germany). The surface morphology and particle size were studied using a Hitachi S-4800 SEM instrument (Hitachi Limited, Japan). Elemental compositions were determined using a Hitachi S-4800 SEM equipped with an INCA 350 energy dispersive spectrometer (SEM-EDS) presenting a 133-eV resolution at 5.9 keV. TEM observation was performed using a Hitachi H-7650 microscope at 80 kV (Hitachi Limited, Japan). Melting points were measured on an X-5 digital melting point apparatus (Gongyi, China) without correction. IR spectra were recorded in the range 4000–600 cm^{-1} using KBr pellets on a Bruker-TENSOR 27 spectrometer instrument (Bruker, Germany). ^1H NMR and ^{13}C NMR spectra were recorded on Zhongke Niujin AS 400 spectrometer (Wuhan, China) at 400 and 100 MHz, respectively, using $CDCl_3$ as the solvent and TMS as an internal standard. Mass spectra were performed on a ThermoFinnigan LCQ Advantage instrument (ThermoFinnigan, USA) with an ESI source (4.5 KeV).

4.2 | Preparation of the POM/MOF-5

The POM/MOF-5 was prepared by the modified procedure.[39] Typically, a mixture of Zn $(NO_3)_2{\cdot}6H_2O$ (0.416 g) and $H_3PMo_{12}O_{40}{\cdot}nH_2O$ (0.2 g) in distilled water (10 mL) was stirred for 15 min, and then H_2BTC (0.174 g) and $(CH_3)_4NOH$ (0.09 g, 1.0 mmol) were added in succession with stirring for another 30 min at room temperature. The turbid mixture was sealed in a Teflonlined stainless steel container and heated at 180°C for 24 h, followed by cooling to room temperature. After removal of the mother liquor from the mixture, crystals were collected and washed with water and EtOH and then dried under vacuum at 125 °C for 6 h.

4.3 | General procedure for the synthesis of poly-functionalized 3-pyrrolin-2-ones

The mixture of aldehyde (1.0 mmol), aniline (2.0 mmol), and dimethyl but-2-ynedioate (1.0 mmol) and POM/MOF-5 (10 mg) in MeOH (2 ml) at room temperature for 1–5 h is monitored by TLC. Upon completion of the reaction, 5 ml of ethyl acetate was added. The product was dissolved in ethyl acetate and the catalyst was separated by simple filtration, washed with ethyl acetate, and used for subsequent cycles after drying under vacuum. Pure product was obtained by evaporation of the solvent, followed by column chromatography on silica gel using ethyl acetate/hexane as the eluent.

4.4 | Characterization data for unknown products

4.4.1 | Methyl 2-(4-ethoxyphenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4c)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.26–7.22 (m, 2H), 7.18–7.13 (m, 5H), 7.08 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 8.5 Hz, 2H), 5.77 (s, 1H), 3.94 (q, J = 7.0 Hz, 2H), 3.53 (s, 3H), 1.35 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.0, 158.7, 141.8, 138.7, 136.5, 128.8, 128.7, 128.5, 128.3, 125.7, 124.7, 122.9, 122.8, 114.3, 109.5, 63.3, 62.7, 51.2, 14.9; IR (KBr): 3201, 3021, 1743, 1625, 1462, 1387, 1260, 1021, 875, 654, 538 cm^{-1}; ESI-MS: m/z = 429.5 $(M + 1)^+$.

4.4.2 | Methyl 2-(4-(*tert*-butyl)phenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4d)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.27 (s, 1H), 7.25–7.23 (m, 3H), 7.18–7.13 (m, 5H), 7.08 (t, J = 7.5 Hz, 1H), 5.80 (s, 1H), 3.54 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.2, 150.9, 141.8,

138.7, 136.7, 133.4, 128.8, 128.5, 127.1, 125.5, 125.4, 124.7, 122.9, 122.5, 109.7, 62.7, 51.2, 34.5, 31.3; IR (KBr): 3387, 3269, 2924, 1721, 1604, 1542, 1443, 1341, 748, 538 cm^{-1}; ESI-MS: m/z = 441.5 $(M + 1)^+$.

4.4.3 | Methyl 2-(4-hydroxyphenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4e)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 3H), 7.31 (t, *J* = 8.0 Hz, 4H), 7.25–7.13 (m, 4H), 7.10 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 5.76 (s, 1H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 155.3, 141.9, 136.4, 128.9, 128.8, 128.6, 128.5, 125.8, 124.8, 123.0, 122.9, 120.9, 115.4, 62.7, 51.2; IR (KBr): 3350, 3053, 1705, 1655, 1406, 1328, 1243, 904, 642, 511 cm^{-1}; ESI-MS: m/z = 401.4 $(M + 1)^+$.

4.4.4 | Methyl 2-(3-fluorophenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4f)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.5 Hz, 2H), 7.28–7.15 (m, 6H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 9.5 Hz, 1H), 6.92–6.85 (m, 1H), 5.80 (s, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.94, 162.5 (d, $^1J_{CF}$ = 244.9 Hz), 142.3, 139.6 (d, $^3J_{CF}$ = 6.7 Hz), 138.4, 136.3, 130.0 (d, $^3J_{CF}$ = 8.1 Hz), 129.0, 128.5, 126.0, 125.0, 123.4, 123.1, 122.7, 115.2 (d, $^2J_{CF}$ = 21.1 Hz), 114.5 (d, $^2J_{CF}$ = 22.1 Hz), 108.5, 62.6, 51.3; IR (KBr): 3387, 3260, 1690, 1602, 1370, 1225, 1031, 853, 682, 513 cm^{-1}; ESI-MS: m/z = 403.4 $(M + 1)^+$.

4.4.5 | Methyl 2-(2-chlorophenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4g)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 18.0, 10.5 Hz, 4H), 7.20 (dd, *J* = 18.0, 10.0 Hz, 4H), 7.15–7.11 (m, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.05–6.98 (m, 1H), 6.50 (s, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 163.9, 142.9, 138.4, 136.3, 135.1, 134.4, 129.7, 129.3, 128.9, 128.5, 127.4, 127.0, 125.8, 125.0, 123.1, 122.3, 108.9, 58.0, 51.3; IR (KBr): 3487, 3269, 1704, 1621, 1433, 1302, 1221, 856, 738, 490 cm^{-1}; ESI-MS: m/z = 419.8 $(M + 1)^+$.

4.4.6 | Methyl 2-(3-chlorophenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4h)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29–7.15 (m, 9H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.78 (s, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.9, 142.4, 139.1, 138.3, 136.2, 134.3, 129.8, 129.0, 128.5, 127.7, 126.0, 125.8, 125.1, 123.2, 122.7, 108.4, 62.5, 51.3; IR (KBr): 3465, 2924, 1735, 1621, 1456, 1328, 1235, 964, 877, 543 cm^{-1}; ESI-MS: m/z = 419.8 $(M + 1)^+$.

4.4.7 | Methyl 5-oxo-1-phenyl-4-(phenylamino)-2-(3-(trifluoromethyl) phenyl)-2,5-dihydro-1*H*-pyr role-3-carboxylate (4j)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.53 (s, 1H), 7.43 (dt, *J* = 13.5, 6.5 Hz, 4H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 1H), 7.20 (d, *J* = 8.5 Hz, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.87 (s, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.8, 142.7, 138.2, 136.1, 130.6, 129.1, 128.6, 126.1, 125.3, 125.1 (q, $^3J_{FC}$ = 3.6 Hz), 124.8 (q, $^3J_{FC}$ = 3.7 Hz), 123.4, 122.8, 108.2, 62.6, 51.3; IR (KBr): 3455, 3307, 2949, 1692, 1637, 1369, 1260, 1120, 932, 769, 532 cm^{-1}; ESI-MS: m/z = 453.4 $(M + 1)^+$.

4.4.8 | 2-(4-cyanophenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4l)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.43–7.39 (m, 3H), 7.34 (dd, *J* = 14.5, 6.5 Hz, 3H), 7.28 (s, 1H), 7.24 (s, 1H), 7.19 (t, *J* = 8.5 Hz, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.86 (s, 1H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 163.8, 142.6, 138.1, 136.0, 132.4, 129.12, 128.5, 128.4, 126.2, 125.3, 123.3, 122.6, 118.5, 112.1, 107.6, 62.5, 51.3; IR (KBr): 3387, 2230, 1701, 1645, 1500, 1372, 1228, 930, 853, 510 cm^{-1}; ESI-MS: m/z = 410.4 $(M + 1)^+$.

4.4.9 | Methyl 5-oxo-1-phenyl-4-(phenylamino)-2-(thiophen-2-yl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4m)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.31 (q, *J* = 8.0 Hz, 4H),

7.20–7.13 (m, 5H), 7.02 (d, J = 3.0 Hz, 1H), 6.83–6.81 (m, 1H), 6.13 (s, 1H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.3, 142.2, 140.8, 138.4, 136.0, 128.9, 128.5, 127.5, 126.5, 126.2, 125.4, 125.0, 123.5, 123.1, 108.3, 58.7, 51.3; IR (KBr): 3388, 3057, 1655, 1466, 1224, 860, 753, 495 cm^{-1}; ESI-MS: m/z = 391.5 $(M + 1)^+$.

4.4.10 | Methyl 2-(5-methylfuran-2-yl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4n)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.42 (d, J = 7.5 Hz, 2H), 7.34–7.29 (m, 4H), 7.17 (dd, J = 13.5, 5.5 Hz, 4H), 6.17 (d, J = 7.0 Hz, 1H), 5.83 (s, 1H), 5.79 (d, J = 2.5 Hz, 1H), 3.61 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.6, 152.2, 146.6, 142.8, 138.5, 136.4, 128.8, 128.4, 126.1, 124.9, 123.4, 123.1, 110.6, 106.4, 105.4, 57.2, 51.3, 13.6; IR (KBr): 3409, 2919, 1624, 1453, 1232, 1352, 1190, 1088, 742, 498 cm^{-1}; ESI-MS: m/z = 389.4 $(M + 1)^+$.

4.4.11 | Methyl 5-oxo-1-phenyl-4-(phenylamino)-2-(pyridin-4-yl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4o)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 4.5 Hz, 2H), 8.25 (s, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 1H), 7.20–7.18 (m, 5H), 7.10 (t, J = 7.0 Hz, 1H), 5.80 (s, 1H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.8, 150.0, 146.6, 142.6, 138.1, 136.0, 129.1, 128.5, 126.2, 125.3, 123.3, 122.6, 122.5, 107.3, 61.9, 51.3; IR (KBr): 3376, 2920, 1607, 1450, 754, 680, 533 cm^{-1}; ESI-MS: m/z = 386.4 $(M + 1)^+$.

4.4.12 | Methyl 2-(naphthalen-2-yl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4p)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.80–7.71 (m, 4H), 7.49 (t, J = 8.5 Hz, 2H), 7.45–7.41 (m, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.27 (dd, J = 8.5, 1.5 Hz, 1H), 7.22–7.15 (m, 5H), 7.03 (t, J = 7.5 Hz, 1H), 5.98 (s, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.1, 142.2, 138.6, 136.5, 134.2, 133.2, 133.2, 128.9, 128.5, 127.9, 127.7, 126.2, 125.8, 124.9, 124.1, 122.9, 109.2, 63.3, 51.25 (s); IR (KBr): 3416, 3250, 2927, 1645, 1611, 1460, 1328, 1205, 750, 552 cm^{-1}; ESI-MS: m/z = 435.5 $(M + 1)^+$.

4.4.13 | Methyl 2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4q)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 13.5, 5.5 Hz, 3H), 7.25 (d, J = 5.0 Hz, 1H), 7.15 (dd, J = 13.0, 7.5 Hz, 3H), 7.09 (t, J = 7.5 Hz, 1H), 6.78–6.67 (m, 3H), 5.71 (s, 1H), 4.18 (s, 4H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 163.9, 143.4, 143.3, 141.9, 138.6, 136.5, 129.7, 128.9, 128.5, 125.7, 124.8, 122.9, 122.8, 120.8, 117.2, 116.2, 109.3, 64.1, 62.5, 51.2; IR (KBr): 3284, 3065, 2950, 1691, 1655, 1436, 1206, 954, 738, 487 cm^{-1}; ESI-MS: m/z = 443.5 $(M + 1)^+$.

4.4.14 | Methyl 5-oxo-1-phenyl-4-(phenylamino)-2-(thiazol-2-yl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4r)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.63 (d, J = 3.0 Hz, 1H), 7.52 (d, J = 7.5 Hz, 2H), 7.36–7.28 (m, 4H), 7.24–7.17 (m, 4H), 7.14 (t, J = 7.5 Hz, 1H), 6.32 (s, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 164.6, 163.2, 143.3, 142.4, 138.0, 135.9, 129.0, 128.5, 126.3, 125.4, 123.5, 123.0, 120.7, 120.3, 105.9, 60.2, 51.5; IR (KBr): 3482, 3065, 1788, 1643, 1426, 1370, 739, 644, 530 cm^{-1}; ESI-MS: m/z = 392.4 $(M + 1)^+$.

4.4.15 | Methyl 1-(3-bromophenyl)-4-((3-bromophenyl)amino)-5-oxo-2-phenyl-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4x)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.77 (s, 1H), 7.34–7.08 (m, 12H), 5.77 (s, 1H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 163.7, 139.7, 137.7, 135.9, 130.1, 129.7, 128.7, 128.5, 127.9, 127.5, 125.9, 125.5, 122.5, 122.0, 121.7, 120.7, 62.9, 51.5; IR (KBr): 3327, 1695, 1621, 1477, 1411, 1024, 810, 676, 539 cm^{-1}; ESI-MS: m/z = 543.1 $(M + 1)^+$.

4.4.16 | Methyl 5-oxo-1,2-di-p-tolyl-4-(*p*-tolylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4z)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.13–7.02 (m, 10H), 5.73 (s, 1H), 3.54 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 164.8, 163.9,

142.50, 137.7, 136.0, 135.3, 134.5, 134.0, 133.9, 129.4, 129.2, 129.0, 127.4, 123.1, 122.7, 108.5, 62.9, 51.1, 21.2, 21.0, 20.9; IR (KBr): 3310, 2946, 1694, 1633, 1377, 1249, 814, 777, 524 cm^{-1}; ESI-MS: m/z = 427.4 $(M + 1)^+$.

4.4.17 | Methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-5-oxo-2-(*p*-tolyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4aa)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.36 (s, 4H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 4H), 5.73 (s, 1H), 3.59 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.7, 141.8, 138.2, 137.5, 135.6, 132.9, 131.9, 131.5, 129.4, 127.3, 124.5, 123.9, 119.0, 118.0, 110.3, 62.9, 51.4; IR (KBr): 3411, 1706, 1677, 1633, 1492, 1366, 1298, 1241, 1075, 922, 844, 493 cm^{-1}; ESI-MS: m/z = 427.4 $(M + 1)^+$.

4.4.18 | Methyl 2-(4-bromophenyl)-5-oxo-1-(*p*-tolyl)-4-(*p*-tolylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4ab)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.12–7.03 (m, 8H), 5.72 (s, 1H), 3.54 (s, 3H), 2.33 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 163.7, 142.8, 136.3, 135.7, 134.9, 133.6, 131.6, 129.5, 129.3, 129.1, 123.3, 122.7, 121.9, 107.5, 62.4, 51.2, 21.0, 20.9; IR (KBr): 3290, 3019, 2252, 1693, 1651, 1399, 1259, 843, 772, 519 cm^{-1}; ESI-MS: m/z = 492.4 $(M + 1)^+$.

4.4.19 | Methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2-(4-chlorophenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4ac)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.42 (q, *J* = 9.0 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 5.80 (s, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 163.5, 142.1, 137.2, 135.2, 134.8, 134.2, 132.1, 131.5, 129.0, 128.8, 124.8, 123.9, 119.2, 118.2, 109.4, 62.1, 51.5; IR (KBr): 3416, 1706, 1631, 1491, 1368, 1295, 1242, 1071, 925, 847, 777 cm^{-1}; ESI-MS: m/z = 577.2 $(M + 1)^+$.

4.4.20 | Ethyl 2-(3-bromophenyl)-5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4af)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.44 (s, 3H), 7.15–6.79 (m, 11H), 5.76 (s, 1H), 4.02 (s, 2H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 163.5, 142.0, 139.0, 138.0, 135.9, 130.9, 130.6, 129.7, 128.7, 128.1, 125.7, 125.6, 124.6, 122.7, 122.3, 121.9, 121.5, 108.5, 62.0, 60.0, 13.5; IR (KBr): 3389, 3079, 1705, 1621, 1466, 1328, 1241, 859, 688, 499 cm^{-1}; ESI-MS: m/z = 478.4 $(M + 1)^+$.

4.4.21 | Ethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-5-oxo-2-phenyl-2,5-dihydro-1*H*-pyrrole-3-carboxylate (4ag)

Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.41–7.10 (m, 13H), 5.80 (s, 1H), 4.08 (s, 2H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 135.3, 132.3, 132.1, 132.24–130.86 (m), 128.8, 128.4, 127.8, 127.4, 124.6, 124.2, 124.0, 123.6, 124.2, 63.1, 60.6, 13.6; IR (KBr): 3364, 3053, 1715, 1648, 1432, 1301, 1257, 1088, 879, 653, 429 cm^{-1}; ESI-MS: m/z = 557.2 $(M + 1)^+$.

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AUTHOR CONTRIBUTIONS

Li Baole: Data curation; investigation. **Hong-Yan Zhang:** Methodology. **Jia-Qi Di:** Methodology. **Zhan-Hui Zhang:** Project administration.

CONFLICT OF INTEREST

There are no conflicts to declare.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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