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Highly Efficient Chemoselective Synthesis of Pyrrolo[2,3-*c*]pyrazole Bearing Oxindole *via* Sequential Condensation–Michael Addition–Intramolecular Cyclization Reactions

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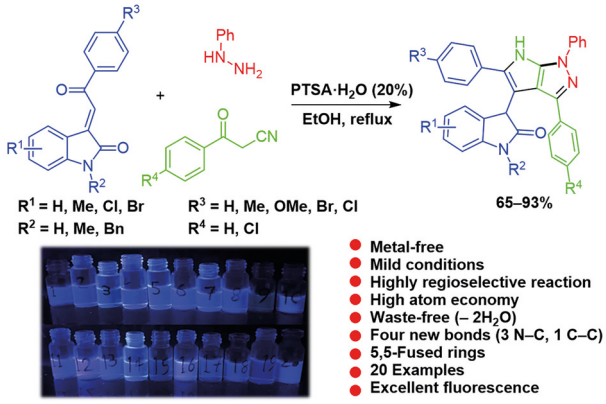

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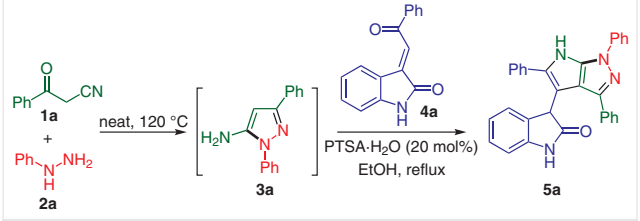
Abstract An efficient and highly chemoselective approach for the synthesis of novel scaffolds based on pyrrolo[2,3-*c*]pyrazole bearing oxindole is accomplished by the acid-promoted sequential reactions between benzoylacetonitriles, phenylhydrazine, and 3-phenacylideneoxindoles as readily available starting materials. This value structure is dexterously embraced with oxindole, pyrrole, and pyrazole heterocycles, which are famous for their enriched biological properties. Besides, this is an eco-friendly and atom-economy approach, and water is the only side product of the reaction. In this protocol, the requirement of column chromatography is completely avoided, and the products were isolated by recrystallization in crude reactions. These compounds due to their excellent fluorescence features and bioactive scaffolds may be attracted great interest in biomedical applications and clinical diagnostics in the future.

Key words oxindole, pyrazole, pyrrole, multicomponent reactions, chemoselective

Pyrazoles and pyrroles have been known as the important classes of five-membered heterocycles, which are present as the basic cores in many pharmaceutical and biologically active compounds and natural products.[1] In addition, pyrrole rings fused to pyrazole rings are an important source of bioactive molecules, which are extensively studied for many applications including antimicrobial agents, antitumor agents, antiviral agents, anti-inflammatory agents, androgen receptor modulators, agents acting on CNS disorders, inhibitors of $K_{ir}3.1$ and $K_{ir}3.4$ potassium channels subunits subtypes, and skeletal muscle contractility modulators.[2]

Oxindoles are privileged heterocyclic scaffolds for the discovery of new drugs and the creation of useful biologically active molecules. These biologically attractive scaffolds exhibited antibacterial and anticancer activity and are inhibitors of Aurora B or bromodomain. In particular, substituted indolin-2-ones act as ligands for dopamine D4 receptor or α-synuclein fibrils (Figure 1).[3]

3-Phenacylideneoxindoles are versatile synthons with multiple reactive sites for the synthesis of heterocycles connected to oxindoles including pyrrole-oxindoles, imidazole-oxindoles, spiro-oxindoles, and furan-oxindoles. These compounds can be obtained from the reactions of isatins and arylethanones. [4] Recently, *N*-heterocyclic rings were employed as fluorescence scaffolds for applications with high-quality demands.[5] In semiconductors, for the preparation of low-bandgap-conjugated polymers or copolymers,[6] pyrrolo-pyrroles are applied in optoelectronics and biophotonics platforms.[7] Particularly Schutting et al. employed pyrrolo-pyrrole dyes as the colorimetric and fluorescent pH



Scheme 1 The model reaction for the synthesis of pyrrolo[2,3-*c*]pyrazole bearing oxindole

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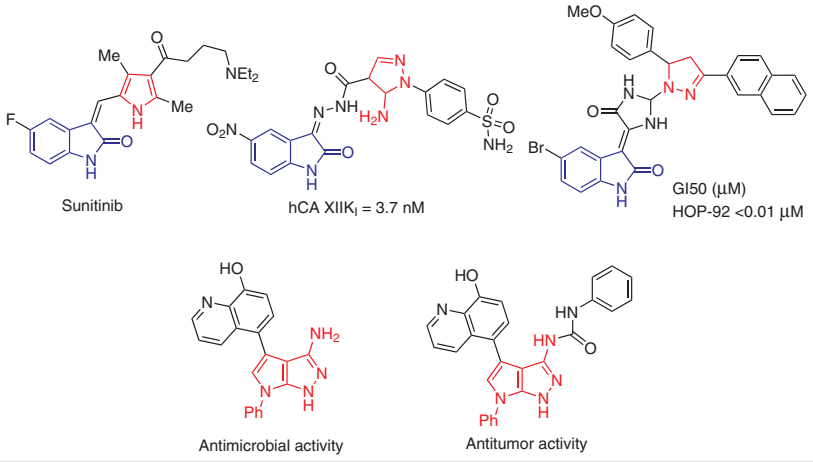


Figure 1 Representative natural products and bioactive compounds

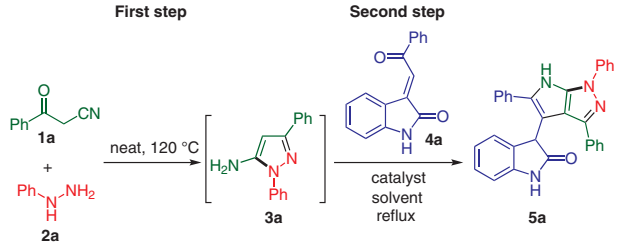
indicators for optical detecting of CO_2.[8] These compounds can be also used for fluorescence imaging in biomedical research and clinical diagnostics.[9]

In continuation of our interest in the synthesis of combinatorial heterocyclic compounds,[10] herein, we report an efficient approach for the synthesis of unusual 5,5-fused ring system bearing oxindole **5a** from the reactions of benzoylacetonitrile (**1a**), phenylhydrazine (**2a**), and 3-phenacylideneoxindole (**4a**, Scheme 1).

This synthetic protocol is carried out in two steps. The first step is the reaction of benzoylacetonitrile (**1a**) with phenylhydrazine (**2a**) under neat conditions at 120 °C. The second step is the reaction of 3-phenacylideneoxindole (**4a**) with 5-aminopyrazole (**3a**), which is formed in the first step. According to our previous report,[11] the optimized conditions for the synthesis of 5-aminopyrazole (**3a**) was used. In a pilot experiment, phenylhydrazine (**2a**) is reacted with benzoylacetonitrile (**1a**) to produce 5-aminopyrazole (**3a**) under neat conditions at 120 °C. Afterwards, 3-phenacylideneoxindole (**4a**) is added to the reaction mixture and investigated under various conditions. The reaction in the second step did not occur in the presence of basic catalysts even under reflux conditions in CH_3CN after 6 h (Table 1, entries 1 and 2). Inorganic acids, such as H_2SO_4 and HCl, had a poor effect on the reaction progress (entries 3 and 4). In continuation, various Lewis acid catalysts such as $InCl_3$, $SnCl_2$, $ZnCl_2$ and an organic acid such as acetic acid were examined and the results showed medium catalytic activity (entries 5–8). Fortified by the results obtained, we examined the reaction in the presence of PTSA·H_2O as a catalyst, and the product **5a** was obtained in an acceptable yield (entry 9). The reaction was carried out in various solvents like CH_3CN, THF, toluene, EtOH, and water. Among all the solvents, ethanol was found to be the optimal medium in terms of the yield and reaction efficiency (entry 13). We proceeded further to optimize the amount of PTSA·H_2O. Subsequently, by increasing the amount of PTSA·H_2O from 10% to 20%, the product **5a** was obtained in an improved yield of 80% after 6 h (entry 15). To test the role of temperature in this strategy, the reaction was performed at different temperatures. By lowering the temperature from reflux to 60 °C or room temperature, the reaction yield decreases to 35% or 0% in 6 h, respectively (entries 20 and 21). It is worth mentioning that the product **5a** was isolated through crystallization based on the crude reaction solvent and no column chromatography technique was used for purification. It should be highlighted that the product **5a** was obtained with complete chemoselectivity.

Upon optimization of the reaction conditions, the reaction of a wide range of 3-phenacylideneoxindoles **4** was investigated. The results are summarized in Scheme 2. As shown, various 3-phenacylideneoxindoles **4** with different kinds of substituents in the oxindole and phenacyl moieties were found suitable for this reaction. Different substituent groups (Cl, Br, and Me) on the oxindole moieties had a good compatibility, and the desired products were obtained in a range of 86–90% yields in a highly chemoselective manner (Scheme 2, 5d, 5n, and **5o**). The effect of *N*-protecting groups of 3-phenacylideneoxindoles **4** was also examined. Interestingly, utilizing of *N*-protecting groups (Me and Bn) had no effect on the chemoselectivity. 3-Phenacylideneoxindoles **4** containing *N*-methyl protecting groups could participate in this reaction very well to provide the corresponding products in a range of 89–93% yields. It is noteworthy that the reaction can also be successfully extended to benzoyl-substituted 3-phenacylideneoxindoles **4**. For example, the benzoyl-substituted component had good com-

Table 1 Optimization of the Second-Step Reaction Conditions[a]



Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%)[b]
1	piperidine (10)	MeCN	6	0
2	Et_3N (10)	MeCN	6	0
3	H_2SO_4 (10)	MeCN	6	trace
4	HCl (10)	MeCN	6	trace
5	$InCl_3$	MeCN	6	35
6	$SnCl_2$	MeCN	6	25
7	$ZnCl_2$ (10)	MeCN	6	30
8	AcOH (10)	MeCN	6	17
9	PTSA·H_2O (10)	MeCN	6	50
10	PTSA·H_2O (10)	H_2O	6	53
11	PTSA·H_2O (10)	THF	6	36
12	PTSA·H_2O (10)	toluene	6	20
13	PTSA·H_2O (10)	EtOH	6	64
14	PTSA·H_2O (10)	EtOH	10	72
15	PTSA·H_2O (20)	EtOH	6	80
16	PTSA·H_2O (20)	EtOH	10	82
17	PTSA·H_2O (15)	EtOH	6	68
18	none	EtOH	6	trace
19[c]	PTSA·H_2O (20)	–	6	46
20[d]	PTSA·H_2O (20)	EtOH	6	35
21[e]	PTSA·H_2O (20)	EtOH	6	0

[a] Conditions: The one-pot and two-step reaction. First step: **1** (0.25 mmol), **2** (0.25 mmol) under neat conditions in 120 °C at 2 h. Second step: **4** (0.25 mmol), 2.5 mL solvent, reflux.
[b] Isolated yields.
[c] 120 °C.
[d] 60 °C.
[e] Room temperature.

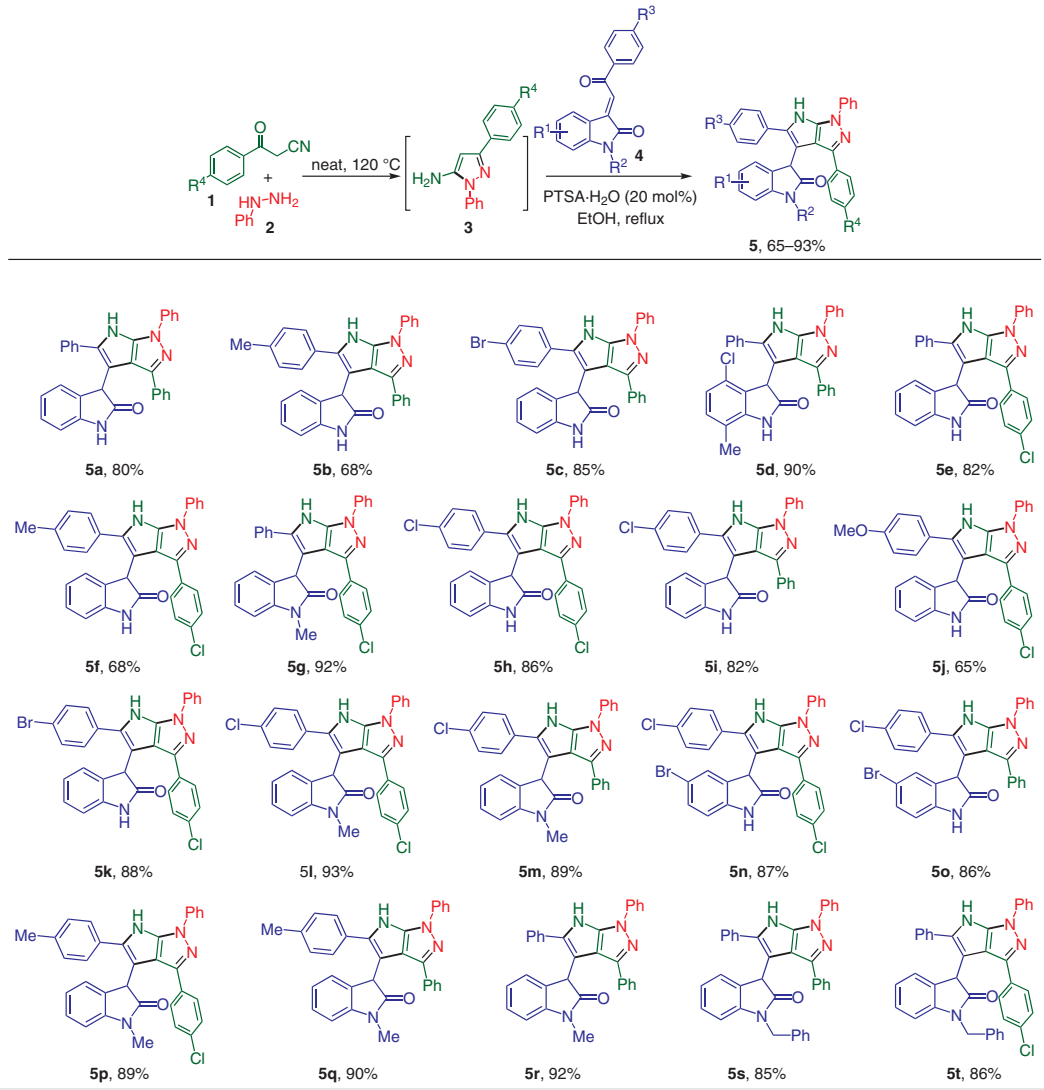
patibility and the desired products **5s** and **5t** were obtained in high yields. In addition, the substituents (such as bromo, chloro, methyl, and methoxy groups) on phenacyl moieties were well tolerated under the reaction conditions and afforded the desired products in satisfactory yields and excellent chemoselectivity. To further explore the versatility of this protocol, the feasibility of changing of benzoylacetonitrile **1** was investigated (Scheme 2). The results revealed that the chloro substituent in position 4 on the aromatic ring was well tolerated under the reaction conditions and afforded the desired products in satisfactory yields.

The reaction of 3-phenacylideneoxindole (**4a**) with 5-aminopyrazole (**3a**) as an intermediate may undergoes several routes on the basis of multiple reactive sites available on compound **4a**[12] (Scheme 3). The reaction, in principle, may generate products **5a**, **6**, or **7** or a mixture of these. Notably, our protocol is completely chemoselective and provides product **5a** exclusively in high yield.

The structure of compound **5g** was confirmed by their analytical and spectral data. In its ^{1}H NMR spectrum at room temperature (Figure 2, a), the singlet appears at δ = 2.98 (3 H) ppm due to the NCH_3 groups. Two singlets at δ = 4.91 (0.88 H) and 5.01 (0.12 H) ppm are the tertiary protons of C-3 on the oxindole moiety, which confirmed the existence of the mixture of tautomers with a ratio of 88:12. The two broad singlets at δ = 11.84 and 11.93 ppm are for NH groups. It is noteworthy that at higher temperature (70 °C) no mixture of tautomers was observed and only a single structure was detected in the ^{1}H NMR spectrum (Figure 2, c). Furthermore, the HMQC spectrum confirms the tautomer structures of **5g** (see Supporting Information). In its ^{13}C NMR, the carbonyl carbons resonated at δ = 176.5 ppm (oxindole carbonyl), two signals in δ = 44.3 ppm corresponds to the carbon located at the third position of the oxindole moiety and δ = 26.5 ppm for NCH_3. The mass spectra of **5g** displayed the molecular ion peak at 514 for M^+ consistent with the molecular structure. Finally, the structure of **5g** was unambiguously verified by single-crystal X-ray analysis, which is shown in Figure 3 (detailed information can be seen in the Supporting Information).

The proposed mechanism for the formation of **5a** is shown in Scheme 4. The first reaction is the condensation of benzoylacetonitrile (**1a**) with phenylhydrazine (**2a**). Afterwards, a chemoselective Michael addition of 5-aminopyrazole (**3a**) to compound **4a** followed by a chemoselective intramolecular cyclization afforded **5a** through the formation **B**, **C**, **D**, and **E** intermediates after final dehydration. The chemoselective Michael addition can be explained by steric hindrance, and the chemoselective intramolecular cyclization is due to the competition between the amide carbonyl and ketone carbonyl of the intermediate **C**.

UV/Vis and photoluminescence (PL) spectroscopy delivers useful information about the structure and the optical properties of the synthesized compounds. As can be seen in Figure 4 (a), the UV/Vis spectra of the pyrrolo[2,3-*c*]pyrazole bearing oxindole derivatives **5** contain maximum absorption at λ = 220 ± 5 and at 335 ± 2 nm. At the C13 and C21 positions of the pyrrolo[2,3-*c*]pyrazole bearing oxindole **5** that bears a chlorine or bromine substituent in the aromatic ring results in a decrement and shift of the absorption maxima to longer wavelengths.



Scheme 2 Substrate scope. Reactions were performed with **1** (0.25 mmol) and **2** (0.25 mmol) under neat conditions in 120 °C at 2 h, afterwards **4** (0.25 mmol), PTSA·H_2O (20 mol %), and ethanol (2.5 mL) were added to the reaction mixture for 6 h.

The PL spectra demonstrated in Figure 4 (b) revealed that the electron-donating group on the aromatic ring at the C13 and C21 positions of the pyrrolo[2,3-*c*]pyrazole bearing oxindole reduce the PL intensity. Also, these compounds show a Stokes shift in the range of 50–65 nm. Digital photographs of synthesized compounds with a concentration of 50 ppm in acetone under UV lamp are depicted in Figure 4 (c, c′, d, and d′). The compound **5p**, which bears a methyl substituent in the aromatic groups, exhibits a high PL intensity at λ = 398 nm.

In summary, we have established a highly efficient approach for the synthesis of novel pyrrolo[2,3-*c*]pyrazoles bearing oxindole from the sequential reactions between phenylhydrazine, benzoylacetonitrile, and 3-phenacylideneoxindole.[13,14] Oxindole, pyrazole, and pyrrole scaffolds in one structure were prepared by chemoselective Michael addition of 5-aminopyrazole, which was *in situ* generated from phenylhydrazine, benzoylacetonitrile to 3-phenacylideneoxindole followed by chemoselective intramolecular cyclization to create diverse products in high yields. This protocol follows an eco-friendly approach and avoids the use of column chromatography for the purification of products. The sequential reactions involve the concomitant removal of the water molecule. In the future, we believe that these fluorescence compounds, due to their bioactive frameworks, may be attracted great attention in the biomedical applications and clinical diagnostics.

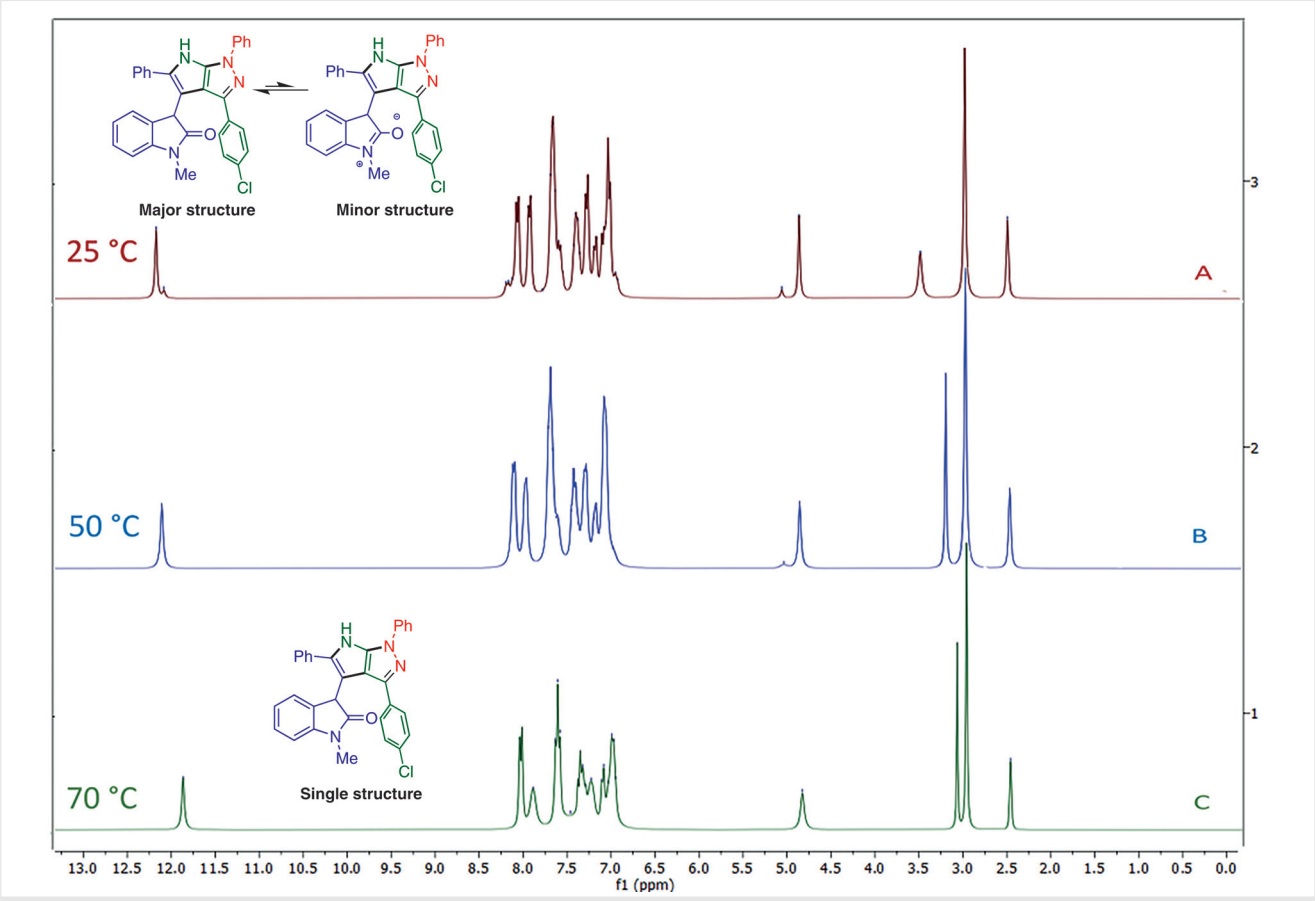


Figure 2 The ^{1}H NMR spectra of **5g** at 25 °C, 50 °C, and 70 °C

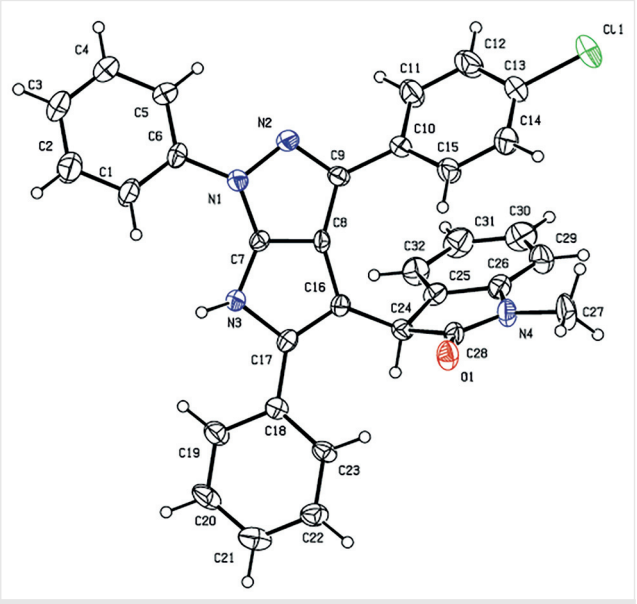
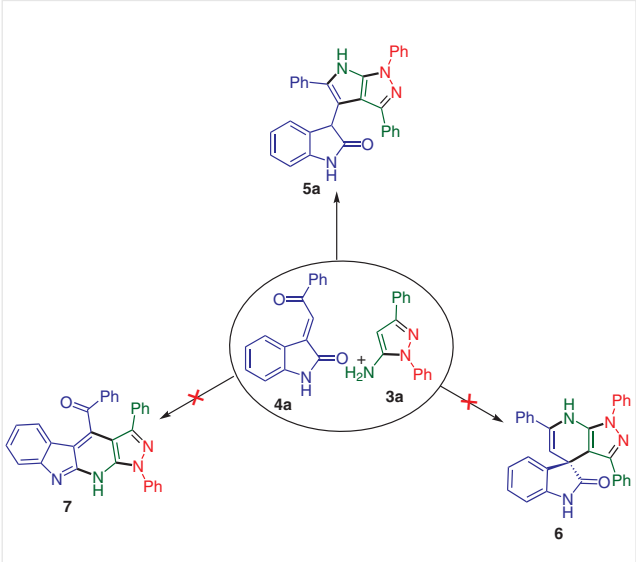
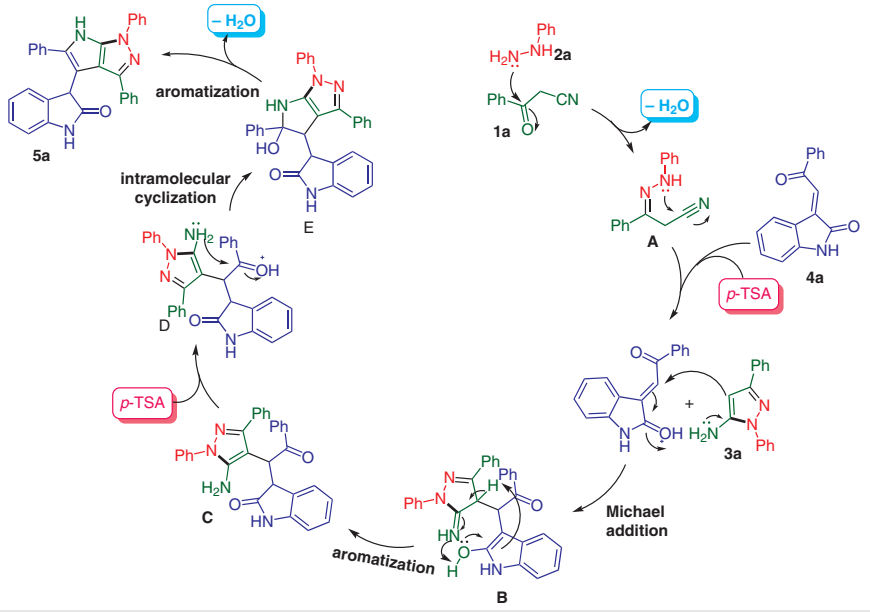


Figure 3 X-ray crystal structure of compound **5g** (CCDC 1974832)



Scheme 3 The model reaction of 3-{1,3,5-triphenyl-1,6-dihydropyrrolo[2,3-c]pyrazol-4-yl}



Scheme 4 Plausible mechanism for the formation of compound **5**

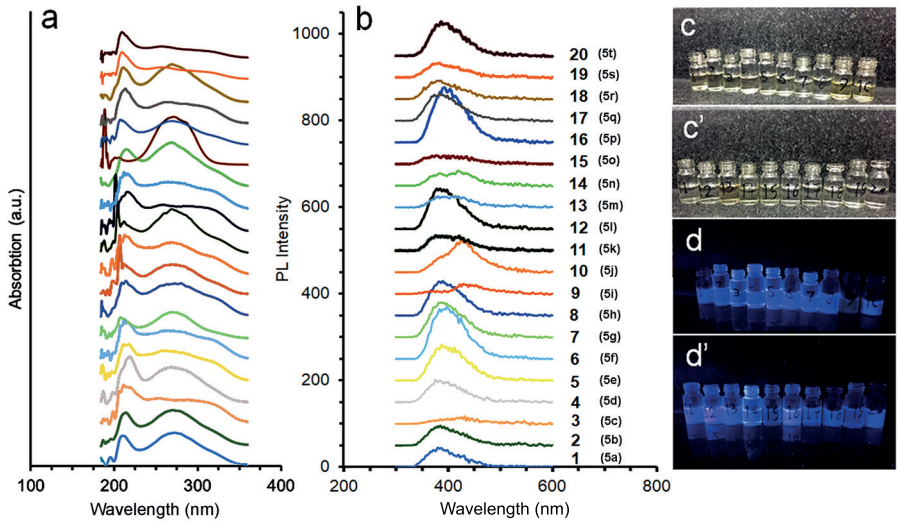


Figure 4 UV/Vis (a) and PL (b) spectra of 50 ppm of synthesized pyrrolo[2,3-c]pyrazole bearing oxindole in acetone, and digital photograph under sunlight (c, c′) and UV light 265 nm (d, d′)

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690887.

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(13) **3-{1,3,5-Triphenyl-1,6-dihydropyrrolo[2,3-*c*]pyrazol-4-yl}indolin-2-one (5a); Typical Procedure**
Benzoylacetonitrile (**1a**, 0.25 mmol) and phenylhydrazine (**2a**, 0.25 mmol) were mixed in neat conditions and heated at 120 °C for 2.0 h. After completion of the reaction, the reaction mixture was cooled to room temperature. Then, 3-(2-aryl-2-oxoethylidene)indolin-2-one (**4a**, 0.25 mmol) PTSA·H_2O (0.05 mmol) and EtOH (2.5 mL) were added to the reaction mixture. Afterwards, the mixture was stirred for 6 h under reflux conditions. Upon the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The precipitate was collected by filtration and washed with cold ethanol to give the pure product **5a** (93 mg, yield 80%).

(14) **3-{1,3,5-Triphenyl-1,6-dihydropyrrolo[2,3-*c*]pyrazol-4-yl}indolin-2-one (5a)**
White powder (92 mg, 80%); mp 214–216 °C. Anal. Calcd (%) for $C_{31}H_{22}N_4O$: C, 79.81; H, 4.75. Found: C, 79.73; H, 4.70. IR (ATR): ν_{max} = 3146 (NH), 1708 (CO), 1467 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (mixture of tautomers) = 4.91 (s, 0.85 H, H_3), 5.16 (s, 0.15 H, H_3), 6.71 (s, 1 H, H_{Ar}), 6.88–6.96 (m, 2 H, H_{Ar}), 7.08–7.28 (m, 10 H, H_{Ar}), 7.39–7.52 (m, 5 H, H_{Ar}), 7.69–7.76 (m, 5 H, H_{Ar}), 8.10–8.23 (br s, 1 H, NH), 8.49 (br s, 1 H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ (mixture of tautomers) = 179.8 (CO), 146.1, 141.6, 141.6, 141.2, 139.3, 133.4, 132.2, 130.2, 129.7, 129.2, 128.7, 128.4, 128.3, 128.2, 127.8, 127.6, 125.5, 124.5, 122.6, 118.6, 115.4, 110.0 (C_{Ar}), 44.9 (C_3). MS (EI, 70 eV): *m/z* = 466 (100) [M^+], 437 (25), 334 (47), 231 (23), 104 (29), 77 (91).