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A rapid, efficient, and novel methodology for the synthesis of 2-aryl-1*H*-phenanthro[9,10-d]imidazole derivatives, catalyzed by bis[*N*-(3,5-dicumylsalicylidene)-2′,6′-fluoroanilinato]zirconium(IV) dichloride under ultrasonic irradiation at room temperature, is reported. A range of substituted imidazoles was synthesized in excellent yields from one-pot reaction of aromatic aldehydes, 9,10-phenanthrenequinone, and ammonium acetate. The remarkable features of this new procedure are introducing a new one-pot method for synthesis of 2-aryl-1*H*-phenanthro[9,10-d]imidazoles, high conversion, short reaction time, and simple experimental and workup procedure.

Keywords 2-aryl-1*H*-phenanthro[9, 10-d]imidazoles, one-pot, Schiff base

INTRODUCTION

Multicomponent reactions (MCRs) have attracted considerable attention since they are performed without need to isolate any intermediate during their processes, which reduces time and saves both energy and raw materials; thus, development and discovery of new MCRs are still in demand.[1–3]

Imidazole and its derivatives are receiving growing attention for their pharmacologically properties, such as herbicidal, fungicidal, analgesic, anti-inflammatory, and antithromobotic activities.[4] During the course of studies on the development of new procedures to synthesize 2,4,5-triarylimidazoles, a number of catalysts, such as copper(II) acetate,[5] Yb(OTf)$_3$,[6] elemental iodine,[7] ZrCl$_4$,[8] HClO$_4$-SiO$_2$,[9] and NiCl$_2$·6H$_2$O,[10] were screened. Some procedures also involve ionic liquid-promoted[11] or microwave assisted synthesis.[12]

However, the development of a simple, efficient, and versatile approach for the preparation of 2,4,5-triarylimidazoles is still an active area of research for further improvements toward milder reaction conditions and higher product yields.

All the reported literature in the field of one-pot synthesis of 2,4,5-triaryl-1*H*-imidazole has examined benzil as a diketone. In the present study, 9,10-phenanthrenequinone instead of benzil was used as a diketone and one-pot, three-component reactions of 9,10-phenanthrenequinone, various aromatic aldehydes, and ammonium acetate in the presence of a catalytic amount of bis[*N*-(3,5-dicumylsalicylidene)-2′,6′-fluoroanilinato]zirconium(IV) dichloride under ultrasonic irradiation have been carried out, and the corresponding 2-aryl-1*H*-phenanthro[9,10- d]imidazoles were obtained in excellent yields whithin short time (Scheme 1). To the best of our knowledge, the one-pot synthesis of 2-aryl-1*H*-phenanthro[9,10-d]imidazole and its derivatives has not been reported up to now. This study provides fast, mild, and efficient method for synthesis of these compounds in a one-pot, three component condensation.

EXPERIMENTAL

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka, and Aldrich chemical companies. All yields refer to isolated products. The reactions were monitored by thin-layer chromatography carried out on silica plates. Infrared (IR) spectra were recorded on a Shimadzu-IR 470 spectrophotometer. ^{1}H-Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 100-MHz spectrometer in dimethyl sulfoxide (DMSO) as the solvent with trimethylsilane (TMS) as internal standard. Flash column chromatography was performed with 300 and 400 meshes silica gel, and analytical thin-layer chromatography (TLC) was performed on precoated silica gel plates (60F-254). Elemental analyses were performed on a Thermo Finnigan EA1112 elemental analyzer. Synthesis of bis[*N*-(3,5-dicumylsalicylidene)-2′,6′-fluoroanilinato]zirconium(IV) dichloride has been reported elsewhere.[13] Scheme 2 shows the synthetic route to the FI Zr-based catalyst.

General Procedure for Preparation of 2-Aryl-1*H*-phenanthro[9,10-d]imidazole Derivatives

A mixture of aromatic aldehyde (1 mmol), 9,10-phenanthrenequinone (1 mmol), and ammonium acetate (3.5 mmol) in CH$_3$CN (10 mL) was stirred at room temperature in the presence of bis[*N*-(3,5-dicumylsalicylidene)-2′,6′-fluoroanilinato]zirconium(IV) dichloride (10 mol%) under ultrasonic irradiation using ultrasonic cleaner with a frequency of 40 kHz and a nominal power 100 W for the appropriate

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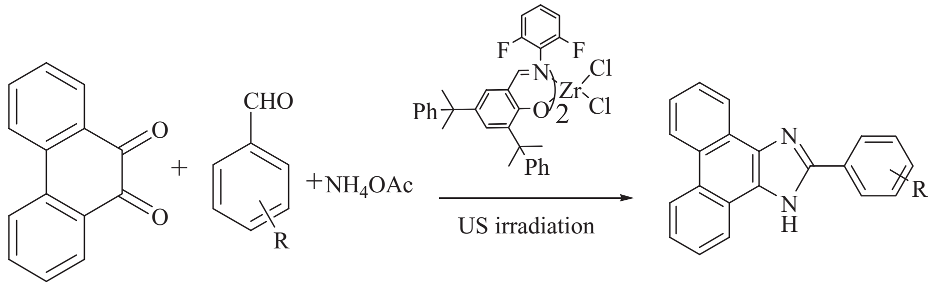
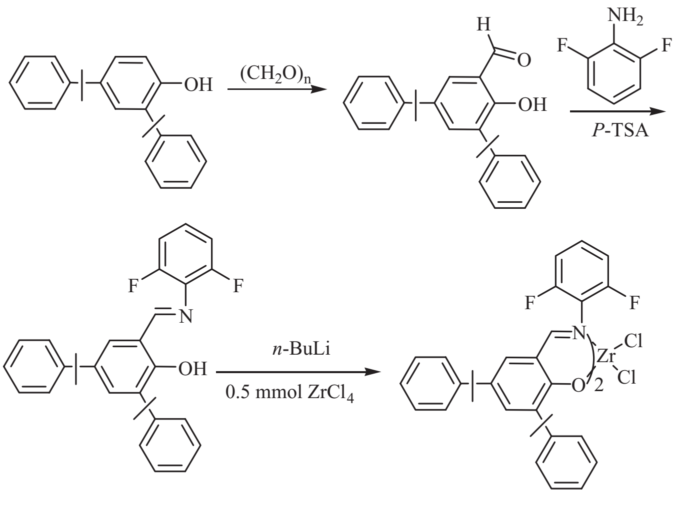


SCH. 1. Synthetic route to imidazol derivatives.



SCH. 2. Synthetic route of the FI Zr-based catalyst.

time (Table 1). After completion of the reaction, as indicated by TLC, the heterogeneous catalyst was filtered out. The obtained crude product was purified by short column chromatography (petroleum ether:ethyl acetate, 9:1) to obtain pure products. The spectra data of the selected compounds are as follows:

2-Phenyl-1*H*-phenanthro[9,10-d]imidazole (**1**): IR (KBr, cm^{-1}): 3405 (N–H), 1552 (C=C), 1590 (C=N). ^{1}H-NMR δ 6.95–7.45 (m, 9H, Ar), 7.75 (d, 2H, J = 7.5 Hz), 8.10 (d, 2H, J = 5.2 Hz), 12.25 (s, NH). Found for $C_{21}H_{14}N_2$: C, 85.33; H, 4.55; N, 9.44%. Calcd: C, 85.69; H, 4.79; N, 9.52%.

2-(4-Nitrophenyl)-1*H*-phenanthro[9,10-d]imidazole (**2**): IR (KBr, cm^{-1}): 3435 (N–H), 1555 (C=C), 1585 (C=N), 1340 (NO_2), 1525 (NO_2). ^{1}H-NMR δ 7.10–7.65 (m, 10H, Ar), 8.04 (d, 2H, J = 8 Hz), 11.95 (s, 1H, NH). Found for $C_{21}H_{13}N_3O_2$: C, 74.25; H, 3.90; N, 12.22%. Calcd.: C, 74.33; H, 3.86; N, 12.38%.

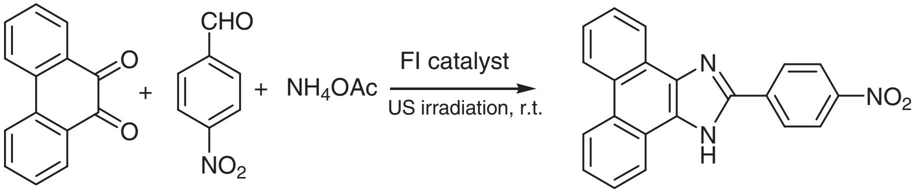
2-(4-Methoxyphenyl)-2*H*-phenanthro[9,10-d]imidazole (**3**): IR (KBr, cm^{-1}): 3405 (N–H), 1552 (C=C), 1590 (C=N). ^{1}H-NMR δ 3.72 (s, 3H), 6.90–7.35 (m, 8H, Ar), 7.88 (d, 2H, J = 7.5 Hz), 8.10 (d, 2H, J = 7.5 Hz), 12.30 (s, NH). Found for $C_{22}H_{16}N_2O$: C, 80.95; H, 4.90; N, 8.55%. Calcd.: C, 81.46; H, 4.97; N, 8.64%.

2-(4-Chlorophenyl)-1*H*-phenanthro[9,10-d]imidazole (**4**): IR (KBr, cm^{-1}): 3420 (N–H), 1425–1540 (C=C), 1595 (C=N). ^{1}H-NMR 7.05–7.55 (m, 8H, Ar), 7.6–7.95 (m, 2H, Ar), 8.10 (d, 2H, J = 7 Hz), 12.14 (s, NH). Found for $C_{21}H_{13}ClN_2$: C, 76.61; H, 3.98; N, 8.46%. Calcd.: C, 76.71; H, 3.99; N, 8.52%.

2-*p*-Tolyl-1*H*-phenanthro[9,10-d]imidazole (**5**): IR (KBr, cm^{-1}): 3405 (N–H), 1425–1525 (C=C), 1605 (C=N). ^{1}H-NMR δ 2.20 (s, 3H), 7.10–7.50 (m, 8H, Ar), 7.70–7.90 (m, 2H, Ar), 8.05 (d, 2H, J = 5.2 Hz), 12.10 (s, NH). Found for $C_{22}H_{16}N_2$: C, 85.60; H, 5.20; N, 8.97%. Calcd.: C, 85.69; H, 5.23; N, 9.08%.

TABLE 1

Influence of the catalyst amount on FI-Zr/US-catalyzed reaction of 9,10-phenanthrenequinone, ammonium acetate, and *p*-nitrobenzaldehyde



Catalyst (mol%)	5%	10%	15%	20%
Yield[a,b]	82	92	93	93

[a] Reaction conditions: CH_3CN (10 ml), *p*-nitrobenzaldehyde (1 mmol), 9,10-phenanthrenequinone (1 mmol), ammonium acetate (3.5 mmol), room temperature and under UV irradiation (6 min).

[b] Isolated yield.

2-(Furan-2-yl)-1*H*-phenanthro[9,10-d]imidazole (**8**): IR (KBr, cm^{-1}): 3410 (N–H), 1415–1530 (C=C), 1608 (C=N). ^{1}H-NMR (100 MHz, DMSO-d6): 7.07–7.55 (m, 7H, Ar), 7.70–8.05 (m, 2H, Ar), 8.35 (d, 2H, J = 5.2 Hz), 12.12 (s, NH). Found for $C_{19}H_{12}N_2O$: C, 80.02; H, 4.21; N, 9.79%. Calcd.: C, 80.27; H, 4.25; N, 9.85%.

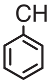
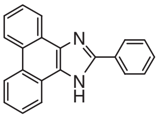
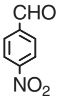
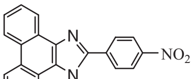
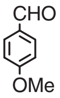
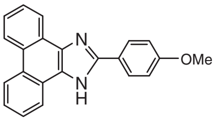
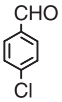
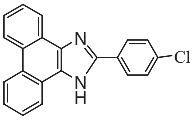
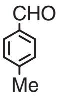
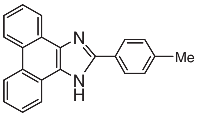
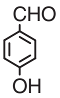
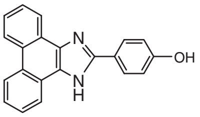
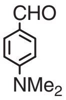
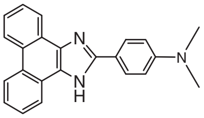
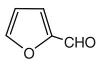
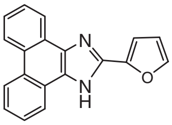
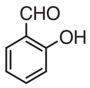
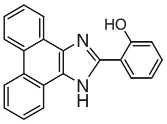
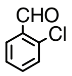
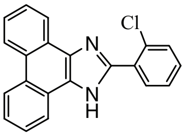
2-(2-Chlorophenyl)-1*H*-phenanthro[9,10-d]imidazole (**10**): IR (KBr, cm^{-1}): IR 3385 (N–H), 1416–1605 (C=C), 1635 (C=N). ^{1}H-NMR δ 7.05–7.50 (m, 4H, Ar), 7.70–8.10 (m, 8H, Ar), 11.95 (s, NH). Found for $C_{21}H_{13}N_2Cl$: C, 76.55; H, 3.91; N, 8.55%. Calcd.: C, 76.71; H, 3.99; N, 8.52%.

RESULTS AND DISCUSSION

As a preliminary study, the reaction of *p*-nitrobenzaldehyde, 9,10-phenanthrenequinone, and ammonium acetate was chosen as a model, and to evaluate the effect of ultrasound for the model reaction, first the reaction was examined without ultrasound at

TABLE 2

Results of 2-phenyl-1*H*-phenanthro[9,10-d]imidazole derivatives synthesis using FI Zr-based catalyst under ultrasonic irradiation

Entry	Aldehyde	Product	Time (min)	Yield (%)[a]
1			45	90
2			45	92
3			55	85
4			45	90
5			50	86
6			50	84
7			55	85
8			50	78
9			40	90
10			60	93

[a]Isolated yields.

room temperature. Moderate yield (58%) with prolonged reaction time (5 h) was found, while with the usage of ultrasound at room temperature a surprisingly excellent yield was found (92%) with a short reaction time (45 min). Therefore, this method was chosen to perform the synthesis of all derivatives of benzochromeno-pyrazoles under ultrasound irradiation. It should be noted that no reaction was observed in the absence of catalyst despite prolonged reaction times.

To optimize the catalyst loading, 5 mol%, 10 mol%, 15 mol%, and 20 mol% of FI catalyst were employed. The yields of 82, 92, 92, and 93% were obtained, respectively. Therefore, 10 mol% loading of FI Zr-based catalyst was sufficient to push the reaction forward.

To generalize the methodology, various starting material were examined and different types of 2-aryl-1H-phenanthro[9,10-d]imidazole were synthesized. Substituted aldehydes bearing electron-withdrawing or electron-donating groups, such as 4-methyl- and 4-methoxy-4-nitrobenzaldehyde, were treated with ammonium acetate in combination with 9,10-phenanthrenequinone under the same experimental conditions, and the corresponding desired products were isolated in excellent yields.

In this method the desired imidazole was obtained without suffering from steric effects; however the reactions took more time (Table 1, entries 10). In this case, a longer reaction time was required to achieve better transformation. As it can be seen in Table 2 (entry 9), salicylaldehyde reacted with ammonium acetate in combination with 9,10-phenanthrenequinone under the same experimental conditions and the corresponding product was obtained in good yield, but the reaction proceeds more rapidly than with other aldehydes used, and the isolated imidazole compound was afforded in a shorter time, due to the intramolecular general acid-catalyzed reaction that facilitates aminal intermediate formation.

The lower chemical yield with heterocyclic aldehyde in comparison with other aldehydes used can be explained by low catalytic activation of furfural carbonyl group by acid, because conjugation with the heterocyclic heteroatom lowers the carbonyl carbon's electrophilicity.

The probable mechanism involves the formation of an aminal intermediate, condensation with 9,10-phenanthrenequinone, which may be catalyzed by the FI catalyst, intramolecular cyclization, and subsequently [1,5] sigmatropic proton shift to afford the corresponding 2-aryl-1H-phenanthro[9,10-d]imidazole derivatives.

CONCLUSION

An efficient, fast and convenient synthesis of 2-aryl-1H-phenanthro[9,10-d]imidazole derivatives accomplished via one-pot, three-component condensations of aryl aldehydes, 9,10-phenanthrenequinone, and ammonium acetate in the presence of bis[N-(3,5-dicumylsalicylidene)-2′,6′-fluoroanilinato]zirconium(IV) dichloride under ultrasonication at room temperature has been described. Applicability of the method for the various compounds, high efficiency of the catalyst system, short reaction times, and high yields of the products prove the merit of this research. Finally, this approach could make a valuable contribution to the existing processes in the field of substituted imidazole synthesis.

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