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ARTICLE

Citrate trisulfonic acid: A heterogeneous organocatalyst for the synthesis of highly substituted Imidazoles

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Citrate trisulfonic acid (CTSA), as a novel recyclable and eco-benign organocatalyst, was employed for the efficient and one-pot synthesis of trisubstituted imidazoles and tetrasubstituted imidazoles using aldehydes, ammonium acetate or aniline, and benzoin, benzyl, or 9,10-phenanthrenequinone under solvent-free conditions providing high to excellent yields. CTSA is easily prepared via the reaction of trisodium citrate and chlorosulfonic acid in high purity. Compared to the conventional procedures, the present method offers several advantages, including high yields, easy work-up, short reaction time, reusability of the catalyst, and simple purification of the products.

KEYWORDS

citrate trisulfonic acid, organocatalyst, reusable catalyst, solvent-free, tetrasubstituted imidazoles, trisubstituted imidazoles

1 | INTRODUCTION

Imidazole and its derivatives form an important class of heterocycles and show a wide variety of biological activities such as herbicidal,[1] antiallergic,[2] analgesic,[3] antidepressant,[4] antitubercular,[5] anticancer,[6] anti-inflammatory,[7] antifungal,[8] and antiviral.[9] They are present in important building blocks including histidine[10] and the related hormone histamine.[11] A number of these ring systems are used in electronic and optoelectronic devices.[12] Trisubstituted imidazoles are used in photography as photosensitive compounds.[13] They are also found to possess high anti-inflammatory activity. Tetrasubstituted imidazoles are active ingredients in many pharmaceuticals including olmesartan, eprosartan, medoxomil, losartan, and trifenagrel.[14]

Imidazole was synthesized for the first time by Heinrich Debus in 1858 from the reaction between glyoxal, formaldehyde, and ammonia.[15] In 1882, poly-substituted imidazole was synthesized using an aldehyde, a 1,2-dicarbonyl compound, and ammonia.[16] In recent years, a number of procedures for the preparation of trisubstituted and tetrasubstituted imidazoles have been reported. 2,4,5-Trisubstituted imidazoles are generally synthesized via the three-component condensation reaction of α-hydroxyketone or 1,2-diketone, ammonium acetate, and an aldehyde in the presence of a strong protic acid such as H_3PO_4,[17] H_2SO_4,[18] or other catalysts in HOAc[19] under reflux conditions, Wells–Dawson heteropolyacid supported on silica (WD/SiO_2),[20] silica gel, or zeolite HY,[21] ionic liquid,[22] $InCl_3$ċ$3H_2O$,[23] $Yb(OTf)_3$,[24] and KH_2PO_4.[25] Tetrasubstituted imidazoles have been obtained by the four-component cyclocondensation of 1,2-diketone, aldehyde, a primary amine, and ammonium acetate using various Lewis or protic acidic reagents such as BF_3-SiO_2,[26] silica gel/$NaHSO_4$,[27] $InCl_3$ċ$3H_2O$-MeOH,[23] HPA-EtOH,[28], L-proline,[29] $K_5CoW^{12-}O_{40}$ċ$3H_2O$,[30] heteropolyacid,[31] zeolite-HY–$Cu(NO_3)_2$,[32] and silica-supported Wells–Dawson acid,[20] hetero-Cope rearrangement,[33] the reaction between 1,2-diketone, a nitrile, and a primary amine under microwave irradiation,[34] and the reaction of 1,3-oxazolium-5-olates with *N*-(arylmethylene) benzenesulfonamides.[35]

Most of the reported literature on the preparation of 2,4,5-triaryl-1*H*-imidazole has examined benzile as a diketone. In this work, we used both benzil and 9,10- phenanthrenequinone as diketones or an α-hydroxyketone. However, most of the existing methods have one or more disadvantages such as expensive catalysts, long reaction time, high cost, and cumbersome work-up procedures.

Consequently, a new method that addresses these drawbacks is of prime importance from both economic and environmental points of view.

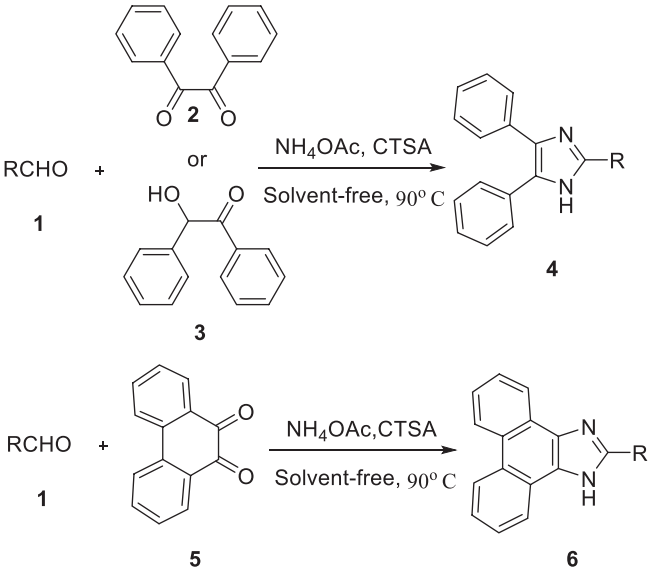
Multicomponent reactions (MCRs) are a useful way to achieve small molecules with diverse structures. In an MCR, three or more components are combined together in one step to produce a final product without the need to isolate any intermediate. Therefore, these reactions reduce the time, save both energy and raw materials, and are useful for the preparation of heterocyclic compounds. Here, the use of heterogeneous organocatalysts can help reduce the amount of toxic waste and byproducts from chemical processes. This group of catalysts has several advantages such as simplicity in handling, low cost, multiple use without loss of efficiency, and simple isolation after the completion of the reaction.[36] In addition, organocatalysts exhibit low toxicity and no sensitivity toward moisture or oxygen.[37] Therefore, development of new, efficient, and eco-friendly organic acidic catalysts with the possibility of reuse is of prime importance in organic synthesis.

In continuation of our efforts on the application of solid acid catalysts, here we report a mild an effective one-pot synthesis of 2,4,5-trisubstituted imidazoles (Scheme 1) and 1,2,4,5-tetrasubstituted imidazoles (Scheme 2) with high efficiency in the presence of citrate trisulfonic acid (CTSA) as a novel organic solid acid catalyst with high catalytic activity and recoverability under solvent-free conditions.

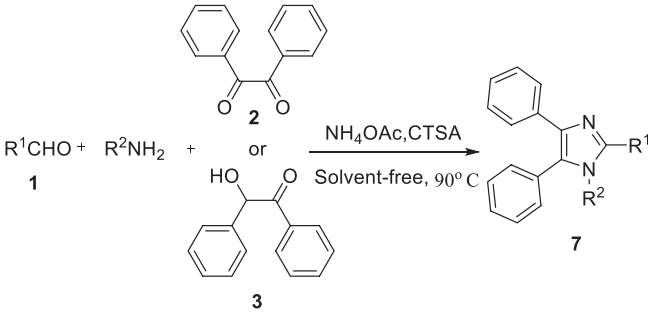
2 | RESULTS AND DISCUSSION

2.1 | Characterization of CTSA

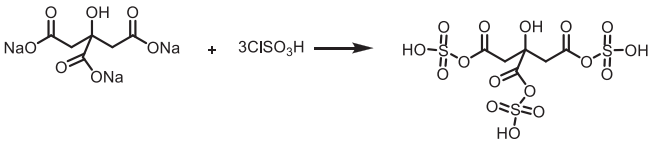
Preparation of an eco-friendly and efficient organic acidic catalyst was attempted, and trisodium citrate was found to be able to react with chlorosulfonic acid to produce CTSA. The procedure of the reaction was very simple, so the product could be synthesized by a simple filtration (Scheme 3).



SCHEME 1 Synthesis of 2,4,5-trisubstituted imidazoles



SCHEME 2 Synthesis of 1,2,4,5-tetrasubstituted imidazoles



SCHEME 3 Synthesis of citrate trisulforic acid

CTSA was characterized by spectroscopic techniques such as IR, ^{13}C NMR, and ^{1}H NMR. In the IR spectrum of trisodium citrate (Figure 1a), the absorption band found at 3,394 cm^{-1} is attributed to the stretching vibration of the OH group. Two absorption bands at 1,606 and 1,585 cm^{-1} are due to the carbonyl groups. The absorption peaks in the region of 1,068–1,442 cm^{-1} are related to the stretching vibration of the C–O group and the bending vibration of the O–H group.

In the IR spectrum of CTSA (Figure 1b), two absorption bands at 3,500–2,468 and 1,643 cm^{-1} are assigned to the stretching and bending vibrations of the OH groups, respectively. The absorption bands in the region between 1,776 and 1,742 cm^{-1} are attributed to the carbonyl groups. The absorption bands at 1,226 and 1,060 cm^{-1} are due to the stretching vibration of S–OH and the asymmetric stretching vibration of S=O of the sulforic acid bonds.

The ^{1}H NMR spectrum of CTSA exhibited two doublets identified as due to the methylene groups (δ = 2.72 and

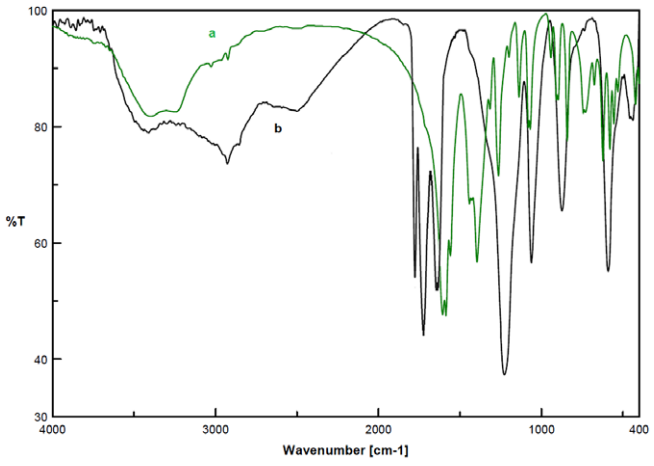


FIGURE 1 FT-IR spectra of (a) trisodium citrate and (b) citrate trisulfonic acid

δ = 2.88 ppm), a broad OH due to the alcohol (δ = 3.87 ppm), and two singlets corresponding to the OH groups of the acid (δ = 12.65 and δ = 12.70 ppm). The proton-decoupled ^{13}C NMR spectrum of CTSA showed four distinct resonances, in agreement with the proposed structure.

2.2 | Recovery and reuse of the catalyst

Recoverability is one of the main characteristics of a heterogeneous catalyst. The recoverability of CTSA was investigated for the model reaction of 4-bromobenzaldehyde, 9,10-phenanthrenequinone, and ammonium acetate**.** After completion of the reaction, the separated catalyst could be recovered after washing with ethanol and drying at 70 °C for 3 hr. It can be seen from Figure 2 that the catalytic system worked well up to four catalytic runs without any significant decrease in the product efficiency and its catalytic activity. Both the fresh and recovered catalysts showed similar FT-IR spectra, indicating that the structure and morphology of the catalyst remained the same after recycling.

2.3 | Effect of solvent, catalyst concentration, and heat on the synthesis of multisubstituted imidazoles

First, in order to optimize the experimental conditions such as solvent, temperature, and the amount of catalyst for the synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles, the condensation between of benzaldehyde (1 mmol), benzil (1 mmol), ammonium acetate (2 mmol for trisubstituted imidazole and 1 mmol for tetrasubstituted imidazole), and 4-chloroaniline (1 mmol for tetrasubstituted imidazole) was selected as the model reaction.

As shown in Table 1, the reaction was screened in ethanol, methanol, water, THF, chloroform, and a solvent-free system, and the best result was obtained after 25 or 34 min under solvent-free conditions for the preparation of trisubstituted and tetrasubstituted imidazoles in excellent yields of 96 and 91%, respectively.

Thereafter, the amount of the catalyst was evaluated in the model reaction, and it was found that a quantitative increase in the amount of CTSA catalyst from 2 to 5 mol% resulted in higher product yields (Table 1, entries 1–3). It is to be noted that further increases in the amount of the catalyst did not lead to any improvement in the reaction rate or yield.

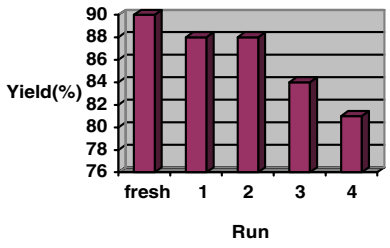


FIGURE 2 Catalytic recyclability of CTSA

TABLE 1 Catalytic activity evaluation and effect of temperature and solvent on the synthesis of multisubstituted imidazoles[a]

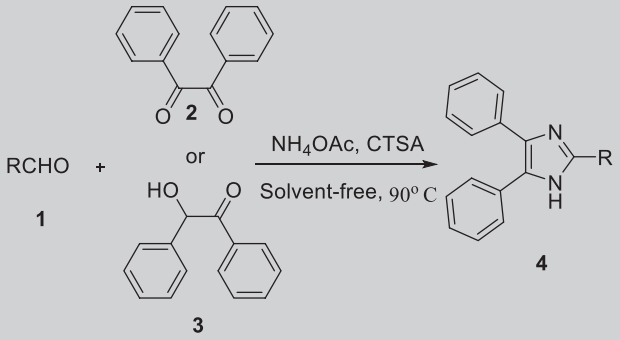
	Conditions A and B[a]			Yield (%)[b]		Time (min)	
Entry	Catalyst (mol. %)	Temp.	Solvent	A	B	A	B
1	2	90	—	74	70	41	58
2	3	90	—	80	77	34	47
3	**5**	**90**	—	**96**	**91**	**25**	**34**
4	10	90	—	91	88	31	40
5	5	Reflux	H_2O	30	32	360	420
6	5	Reflux	EtOH	43	41	180	240
7	5	Reflux	MeOH	35	30	320	380
8	5	Reflux	$CHCl_3$	50	40	380	390
9	5	Reflux	CH_3CN	32	28	340	360
10	5	40	—	69	66	110	120
11	5	70	—	83	70	40	60
12	5	100	—	90	83	35	56
13	5	120	—	95	89	35	40

[a] Reaction conditions: benzaldehyde (1 mmol), benzil (1 mmol), ammonium acetate (2 mmol) for trisubstituted imidazole (condition A); and benzaldehyde (1 mmol), benzil (1 mmol), ammonium acetate (1 mmol), and aniline (1 mmol) for tetrasubstituted imidazole (condition B).
[b] Isolated yields.

After optimization of the catalyst amount and solvent, to improve the yield and decrease the reaction time, the effect of temperature was studied. The result indicated that a temperature of 90 °C led to improvement in the reaction time and yield, while above 90 °C (Table 1 entries 10–13) the reaction preceded smoothly.

With the optimized conditions, we proceeded to investigate the general scope and generality of this method using a wide range of aromatic, heterocyclic, and aliphatic aldehydes as well as benzil or benzoin, and 9,10-phenanthrenequinone. As shown in Table 2, an aldehyde (1 mmol), benzil or benzoin (1 mmol), and ammonium acetate (2 mmol) were readily converted to the corresponding 2,4,5-trisubstituted imidazoles in good to excellent isolated yields over short reaction times under the optimized conditions. To study the substituent effect under optimized reaction conditions, a wide range of aromatic aldehydes containing an electron-withdrawing (i.e., Cl, Br, and NO_2) or electron-donating (i.e., CH_3, OCH_3, and OH) group were used. It was found that aromatic aldehydes having electron-donating groups on the aromatic ring react more slowly than those with electron-withdrawing groups (Table 2). In the presence of aliphatic aldehydes, the reaction resulted in moderate yield at a low reaction rate (Table 2, entry 12). In the same reactions, benzoin (**3**) used instead of benzil (**2**) exhibited lower reactivity (Tables 2 and 3). Also, the optimized conditions for the preparation of phenanthro[9,10-d]imidazoles (**6**) using 9,10-phenanthrenequinone (**5**) gave products in good to excellent yields in short reaction times (Table 4).

TABLE 2
Preparation of 2,4,5-trisubstituted imidazoles catalyzed by CTSA using benzil (**2**) or benzoin (**3**)

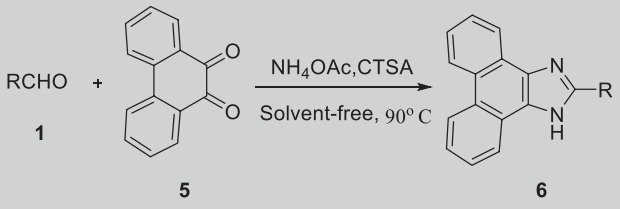


Entry	R	Product	Time (min) Benzil (benzoin)	Yield[a] (%) Benzil (benzoin)	M.p. (°C) Found	Reported
1	C_6H_5	**4a**	25 (35)	96 (93)	271–273	271–272[38]
2	4-$NO_2C_6H_4$	**4b**	24 (33)	92 (91)	240–242	241–242[38]
3	3- $NO_2C_6H_4$	**4c**	24 (39)	89 (88)	267–270	269–271[39]
4	4-ClC_6H_4	**4d**	20 (33)	93 (92)	263–264	260–262[40]
5	2,4- ClC_6H_3	**4e**	26 (32)	88 (86)	173–175	174–175[40]
6	4-Br C_6H_4	**4f**	27 (31)	92 (90)	265–266	264–266[3]
7	4-$OCH_3C_6H_4$	**4g**	35 (44)	84 (84)	231–232	230–232[41]
8	4-$CH_3C_6H_4$	**4h**	37 (45)	81 (80)	232–235	233–234[42]
9	4-OHC_6H_4	**4i**	32 (36)	83 (81)	232–234	233–235[42]
10	4-HO-3-$EtOC_6H_3$	**4j**	40 (48)	87 (86)	260–263	261–263[3]
11	2-Furyl	**4k**	43 (51)	79 (80)	233–234	233–235[29]
12	$CH_3CH_2CH_2$	**4l**	56 (62)	74(71)	204–206	206–208[29]

[a] Isolated yields.

A plausible mechanism for the preparation of imidazoles using aldehyde, benzil, and ammonium acetate is given in Scheme 4. The first step in this reaction involves the CTSA-catalyzed formation of diamine intermediate **8** stabilized by CTSA. Then, the diamine, which is very prone to react with a diketone, leads to the intermediate **10**, which rearranges

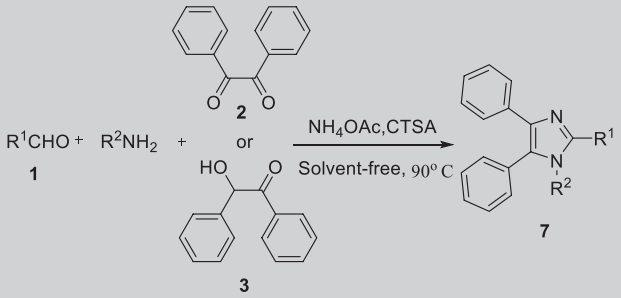
TABLE 3 Preparation of 2,4,5-trisubstituted imidazoles catalyzed by CTSA using 9,10-phenanthrenequinone (5)



Entry	*R*	Product	Time (min)	Yield[a] (%)	M.p. (°C) Found	Reported
1	C_6H_5	**6a**	22	94	323–325	322–324[45]
2	4-$NO_2C_6H_4$	**6b**	25	91	336–339	337–339[3]
3	4-ClC_6H_4	**6c**	23	95	274–275	275–276[45]
4	2,4- ClC_6H_3	**6d**	25	89	224–227	—
5	4-Br C_6H_4	**6e**	26	90	257–259	—
6	4-$OCH_3C_6H_4$	**6f**	26	87	253–254	254–256[3]
7	4-$CH_3C_6H_4$	**6i**	33	88	268–270	268–270[3]
8	4-OHC_6H_4	**6j**	28	91	346–348	348–350[3]
9	5-Br-2-OH C_6H_4	**6k**	27	89	255–257	—

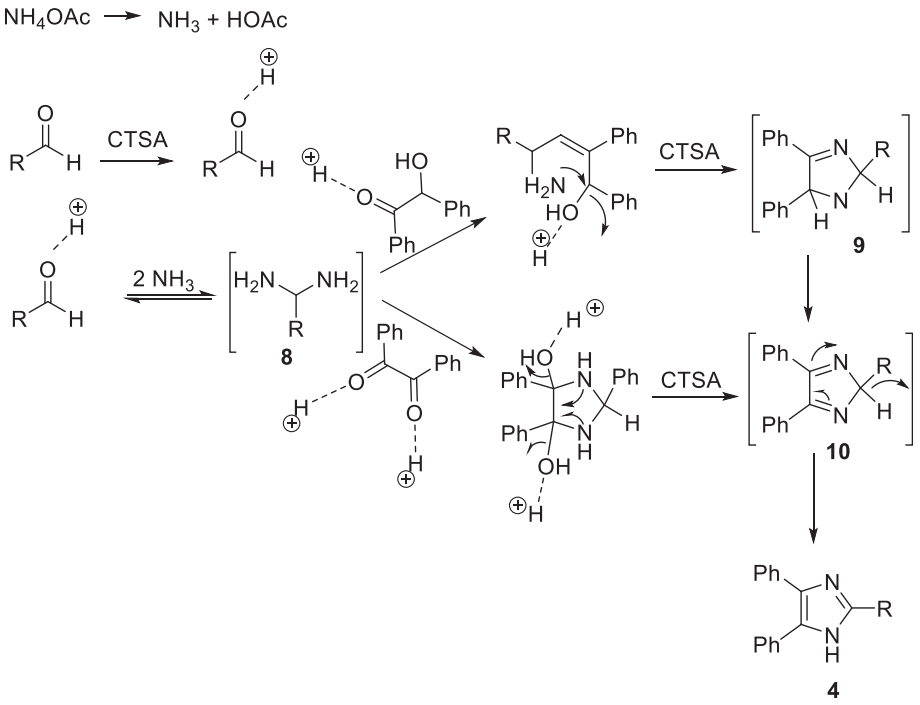
[a] Isolated yields.

TABLE 4 Catalytic synthesis of 1,2,4,5-tetrasubstituted imidazoles using CTSA and benzil or benzoin



Entry	R^1	R^2	Product	Time (min) Benzil (benzoin)	Yield[a] (%) Benzil (benzoin)	M.p. (°C) Found	M.p. (°C) Reported
1	C_6H_5	4-ClC_6H_4	**7a**	34 (39)	91 (89)	197–199	198–199[2]
2	4-$NO_2C_6H_4$	C_6H_5	**7b**	39 (47)	87 (85)	184–187	184–186[3]
3	3- $NO_2C_6H_4$	4-$CH_3C_6H_4$	**7c**	40 (47)	87 (88)	146–149	149–151[30]
4	4-ClC_6H_4	C_6H_5	**7d**	40 (50)	88 (89)	163–165	164–166[43]
5	4-Br-C_6H_4	C_6H_5	**7e**	41 (47)	88 (81)	151–154	152–154[44]
6	4-$OCH_3C_6H_4$	4-ClC_6H_4	**7f**	48 (53)	85 (81)	176–178	176–177[2]
7	4-$CH_3C_6H_4$	C_6H_5	**7g**	50 (55)	86 (81)	186–189	186–188[43]
8	4-OHC_6H_4	C_6H_5	**7h**	42 (53)	85(83)	288–289	285–286[43]

[a] Isolated yields.



SCHEME 4 Possible mechanism for the catalytic synthesis of four highly substituted imidazoles using CTSA

via a [1,5]-sigmatropic proton shift to produce the corresponding imidazole.

On the other hand, the intermediate **8** reacts with benzoin to produce the intermediate of dihydroimidazole **9**, which undergoes aerobic oxidation to form the fully conjugated system **10** and consequently rearranges via a [1,5]-sigmatropic proton shift to give the final product.

3 | EXPERIMENTAL

3.1 | Chemicals and apparatus

All reagents were purchased from Merck, Fluka, and Aldrich chemical companies. Melting points were recorded on a Barnstead Electrothermal (BI 9300) apparatus and are

uncorrected. NMR spectra recorded on a Bruker 400 MHz Ultrashield spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C), with DMSO-d_6 as the solvent and trimethylsilane (TMS) as the internal standard. IR spectra were recorded on a JASCO-680 FT-IR spectrometer.

3.2 | Preparation of citrate trisulfonic acid

Trisodium citrate was obtained by drying trisodium citrate trihydrate in an oven at 250 °C for 6 h to remove the adsorbed water. To chlorosulfonic acid (23.1 mL, 0.3 mol, 34.8 g) in a 250-mL round bottom flask, dried trisodium citrate (25.8 g, 0.1 mmol) was added slowly under vigorous stirring over a period of 30 min at room temperature. After the completion of the addition, the reaction mixture was shaken for 30 min. CTSA was obtained as a light brown solid after washing with hot methanol. Finally, CTSA was dried and stored in a capped bottle.

3.3 | Spectral data of CTSA

M.p. = 190–192 °C; IR (KBr, cm^{-1}): 439, 592, 873, 1,060, 1,226, 1,643, 1,724, 1,776, 2,468, 2,921, 3,500; ^{1}HNMR (400 MHz, DMSO-d_6): δ_H ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 2.72 (d, 2H, J = 15.6 CH_2), 2.88 (d, 2H, J = 15.6 Hz, CH_2), 3.87 (br, 1H, OH), 12.65 (s, 2H, S-OH), 12.70 (s, 1H, S-OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 50.13, 79.41, 188.32, 191.23. MS (*m/z*): 430.4 $[C_6H_8S_3O_{16}]^+$, 337.1 $[C_6H_8S_2O_{12}]^+$, 382.2 $[C_6H_6S_3O_{13}]^+$, 175.1 $[C_6H_8O_6]^+$, 310.1 $[C_5H_8S_2O_{11}]$, 293.1 $[C_5H_8S_2O_{10}]$, 249, 232, 182, 123, 78.

3.4 | General procedure for the preparation of multisubstituted imidazoles

A mixture of benzile or 9,10-phenanthrenequinone or α-hydroxyketone (1 mmol), the corresponding aldehyde (1 mmol), ammonium acetate (2 mmol for 2,4,5-trisubstituted imidazoles and 1 mmol for 1,2,4,5-tetrasubstituted imidazoles) or aniline (1 mmol for 1,2,4,5-tetrasubstituted imidazoles), and CTSA (5% mmol) was stirred in an oil bath at 90 °C for a suitable time. After its completion, as indicated by TLC, hot ethanol (5 mL) was added and the heterogeneous catalyst was separated by filtration. The solvent was evaporated and the obtained crude product was purified by column chromatography or recrystallization from ethanol to afford pure products (Tables 2 and 4). Then, the products were characterized by spectroscopic techniques such as IR, ^{1}H NMR, and ^{13}C NMR and also by comparison of their melting points with those reported in the literature. The data of some new compounds are shown below:

3.5 | 2-(2,4-Dichlorophenyl)-1*H*-phenanthro[9,10-d] imidazole (6e)

Milky solid, m.p. 224–227 °C; IR (KBr) cm^{-1}: 723, 815, 1,103, 1,457, 1,623, 3,428; ^{1}H NMR (400 MHz, DMSO-d_6): 7.88 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.8 Hz, aromatic CH), 7.99 (d, 1H, J = 2.8 Hz, aromatic CH), 8.00–8.02 (m, 5H, aromatic CH), 8.42 (d, 2H, J = 8.8 Hz, aromatic CH), 8.63 (d, 2H, J = 7.6 Hz, aromatic CH), 13.68 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 122.19, 125.64, 125.99, 126.13, 126.41, 127.80, 128.18, 129.61, 131.67, 131.87, 136.01, 136.18, 136.21, 148.03; MS (*m/z*): 363.1 $[C_{21}H_{12}Cl_2N_2]^+$, 328.1 $[C_{21}H_{13}ClN_2]^+$, 294.1 $[C_{21}H_{14}N_2]^+$, 193.1 $[C_{14}H_{11}N]^+$, 264.1, 181.2, 164.1, 118.7, 75.1.

3.6 | 2-(4-Bromophenyl)-1*H*-phenanthro[9,10-d] imidazole (6f)

Yellow solid, m.p. 257–259 °C; IR (KBr) cm^{-1}: 646, 786, 979, 1,087, 1,151, 1,496, 1,519, 1,614, 3,407; ^{1}H NMR (400 MHz, DMSO-d$_6$): 7.68–7.69 (m, 4H, aromatic CH), 7.86–7.88 (m, 4H, aromatic CH), 8.32 (d, 2H, J = 8.4 Hz, aromatic CH), 8.54 (d, 2H, J = 8.0 Hz, aromatic CH), 13.58 (s, 1H, NH); ^{13}C NMR (100 MHZ, DMSO-d$_6$): 120.21, 121.72, 124.87, 125.61, 125.79, 125.80, 129.05, 128.00, 133.67, 133.75, 134.40, 134.50, 135.75, 147.79. MS (*m/z*): 373.1 $[C_{21}H_{13}BrN_2]^+$, 283.2 $[C_{21}H_{17}N]^+$, 207.1 $[C_{15}H_{13}N]^+$, 178.1 $[C_{14}H_{10}]^+$, 294.1, 186.1, 164.1, 146.1, 132.1, 50.1.

3.7 | 4-Bromo-2-(1*H*-phenanthro[9,10-d]imidazol-2-yl) phenol (6k)

Brown solid, m.p. 255–257 °C; IR (KBr) cm^{-1}: 615, 754, 1,232, 1,477, 1,590, 1,668, 3,288. ^{1}H NMR (400 MHz, DMSO-d_6): 7.07(dd, 1H, J_1 = 6.4 Hz, J_2 = 2.4 Hz, aromatic CH), 7.53 (d, 1H, J = 2.4 Hz, aromatic CH), 7.70 (d, 1H, J = 6.4 Hz, aromatic CH), 8.02–8.04 (m, 4H, aromatic CH), 8.51 (d, 2H, J = 8.0 Hz, aromatic CH), 8.88 (d, 2H, J = 7.6 Hz, aromatic CH), 9.19 (brs, 1H, OH), 13.77 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 115.36, 119.91, 122.21, 122.59, 125.84, 126.22, 126.53, 126.91, 128.56, 129.78, 135.75, 135.88, 148.18, 157.03. MS (*m/z*): 389.1 $[C_{21}H_{13}BrN_2O]^+$, 373.1 $[C_{21}H_{13}BrN_2]^+$, 310.1 $[C_{21}H_{14}N_2O]^+$, 294.2 $[C_{21}H_{14}N_2]^+$, 207.1, 164.1, 150.1, 118.1, 102.1, 50.1.

4 | CONCLUSIONS

In this paper, we presented an efficient, fast, and convenient synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles in a one-pot four-component condensation of benzyl, benzoin, or 9,10-phenanthrenequinone with an aldehyde, ammonium acetate, and/or aniline under solvent-free conditions in the presence of CTSA as a recyclable and eco-benign organocatalyst. This method provided the desired products with short reaction times, high efficiency, low cost, reusability of the catalyst, and simple purification of the products.

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