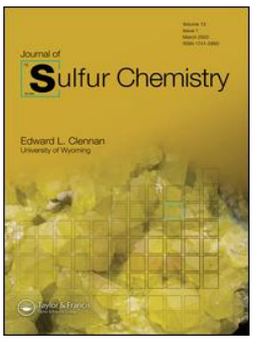

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Condensation–cyclization reaction for one-pot synthesis of 1,3-thiazolidin-4-one derivatives by poly(*p*-phenylenediamine) grafted on LDHs as a catalyst with green tool

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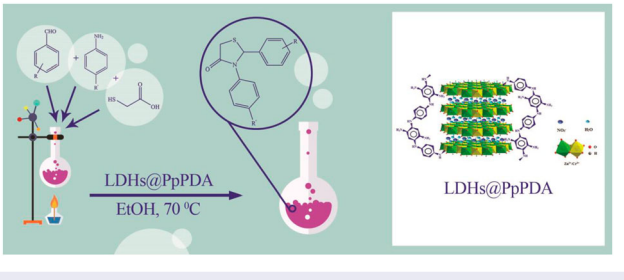
ABSTRACT

The three-component reaction between amine, carbonyl compound and thioglycolic acid is now considered as a major strategy for synthesis of 1,3-thiazolidin-4-ones, which consists of the following steps: (i) condensation of aldehyde and amine which results the formation of an imine; (ii) the reaction between thioglycolic acid and the imine which is followed by an intramolecular cyclization reaction, which leads to the formation of the final product. In this way, if no suitable catalyst is employed, the completion of the reaction will not be achieved. Hence, it is of great importance to select an appropriate catalyst so that these compounds can be successfully synthesized. Herein, we employed LDHs@PpPDA as a versatile catalyst for the fabrication of novel derivatives of 1,3-thiazolidin-4-one.



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Synthesize; condensation; intramolecular cyclization; thioglycolic acid; 1,3-thiazolidin-4-ones

1. Introduction

In heterocyclic compounds, which are regarded as a main category in the field of organic chemistry and take a significant part in both pure and applied chemistry, some or all the atoms present in their molecules are joined together in rings which not only contain carbon atoms but also consist of at least one atom of other elements. They are

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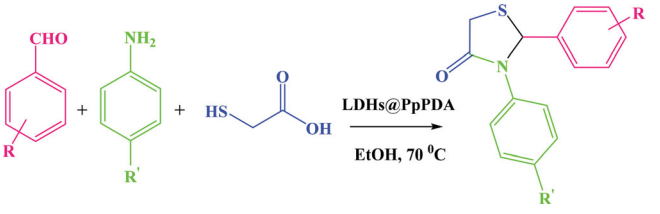
considered as one of the largest groups of organic chemistry materials which are widely employed in numerous applications, *e.g.* the fabrication of pharmaceutical compounds [1] along with intermediates for preparation of the drugs which present antivirals, antibiotics, anti-tumors, antimicrobials, anti-inflammatories, antifungals, and antidiabetics activities [2].

Multi-component reactions (MCRs) are very appropriate for construction of the heterocyclic cores [3,4]. MCRs include reactions in which three or more starting materials react in a one-pot process to form a new product. The advantages of MCRs extend from high atom economy, the ability to build complex molecules, avoiding the necessity of isolation and purifications of the intermediates, consistency with the principles of green chemistry, operational simplicity, and minimizing waste, labor, and cost [5–9].

Thiazolidine-4-one is a five-membered heterocyclic ring with N and S heteroatoms and one carbonyl group, utilized in many strategies for fabrication of the pharmaceuticals, and therefore, it is present in the structure of the fabricated medicines [10–13]. Nowadays, innumerable studies have been carried out around the world to investigate the biological activity of thiazolidine-4-one, whose extensive applications have been demonstrated in a variety of domains, *e.g.* anti-HIV [14–18], antimicrobials [19,20], antihistamines [21,22], anti-YFV (Yellow fever virus) [23], anti-cancers [24], anti-inflammatories [25], and antioxidants [26]. It is noticeable that the fabrication of assorted derivatives with various biological properties can be carried out by modification of the substitutions which exist in the structure of the compounds. For example, Rawal *et al.* could introduce a type of derivatives named 2,3-diaryl-1,3-thiazolidin-4-one, which is a vital drug for the therapy of the HIV virus [16]. Regarding the above-mentioned importance and applications of thiazolidinones in pharmaceutical industry and commercial markets, finding the superior synthesis approaches is very important. So far, innumerable approaches have been proposed by researchers for the fabrication of thiazolidinediones, among which there is a commonly employed strategy which consists of one-pot three-component condensation of amine, the carbonyl compound and thioglycolic acid. According to the literatures, various conditions and catalysts have been investigated in this reaction. For instance, in 2002, Srivastava *et al.* [27] synthesized 4-thiazolidinones by using DCC catalyst and THF solvent in room temperature. In another study which was reported in 2013, Foroughifar *et al.* could synthesize 1,3-thiazolidin-4-ones at 70°C in solvent-free conditions by using $Bi(SCH_2COOH)_3$ as a catalyst [28]. In another work reported in 2016, Safaei-Ghomi *et al.* fabricated novel derivatives of these compounds by using nano-sized $CdZr_4(PO_4)_6$ catalyst under ultrasonic irradiation [29]. Herein, we decide to fabricate innovative derivatives of 1,3-thiazolidin-4-one in agreement with green chemistry. The schematic illustration of



Scheme 1. Synthesis of 1,3-thiazolidin-4-ones catalyzed by LDHs@PpPDA.

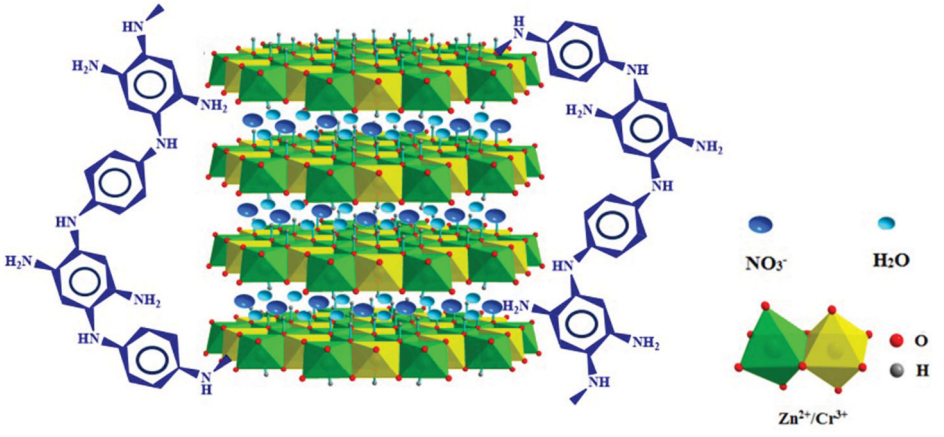


Figure 1. The structure of LDHs@PpPDA.

the synthesis route is exhibited in Scheme 1. As presented in Figure 1, LDHs@PpPDA [30] was utilized as a catalyst for this reaction and the advantages of this is its facile synthetic steps, available raw materials, recyclability and cost-efficiency.

2. Results and discussion

Organic chemists have made numerous efforts to find out the reactions which follow the principles of green chemistry. Therefore, this is very important to consider all the parameters which effect on the expansion of such reactions. Herein, we describe the synthesis of 1,3-thiazolidin-4-ones through the condensation reaction of substituted aldehydes, amine and thioglycolic acid in the presence of LDHs@PpPDA.

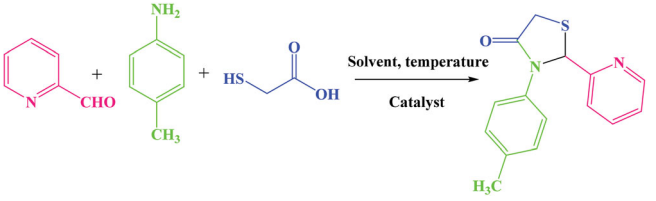
In this work, the reaction among 2-pyridinecarbaldehyde, 4-methyl aniline and thioglycolic acid has been selected as a model reaction, and the effects of various parameters including temperature, solvent, and catalyst have been investigated. At the First, the effect of a variety of catalysts was investigated for the synthesis of 1,3-thiazolidin-4-ones, as depicted in Table 1, based on which, the LDHs@PpPDA catalyst was the foremost efficient catalyst in this synthesis approach.

Numerous effective basic sites were provided in the catalyst by $-NH_2$ and –NH groups, which lead to the superior catalytic activity of LDHs@PpPDA. The reaction conditions, including solvent, temperature and catalyst content, were optimized and listed in Table 2, based on which it was demonstrated that no reaction observed in the absence of the catalyst

Table 1. Comparison of various catalysts for the synthesis of 1,3-thiazolidin-4-one derivatives.

Entry	Catalyst	Solvent	Temp. (°C)	Time (min)	Yield (%)	Ref.
1	MNPs@SiO_2-IL	–	70	60	94	[31]
2	$Bi(SCH_2COOH)_3$	–	70	120	75	[28]
3	DDC	THF	r.t.	50	91	[27]
4	Nano-$CdZr_4(PO4)_6$	PhMe	Ultrasonic irradiation	25	88	[29]
5	Fe_3O_4/SiO_2/Salen/Mn/IL	–	r.t.	50	94	[32]
6	LDHs@PpPDA	EtOH	70	90	95	This work

Table 2. Optimization of the reaction conditions for the synthesis of 1,3-thiazolidin-4-one derivatives using the LDHs@PpPDA catalyst.



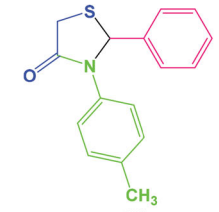
Entry	Catalyst	Solvent	Temp. (°C)	Time (min)	Yield (%)
1	0.05	H_2O	Reflux	240	42
2	0.05	EtOH	70	90	95
3	0.05	CH_2Cl_2	25	240	38
4	0.05	PhMe	70	240	20
5	0.05	Solvent-free	70	240	53
6	0.05	DMF	70	240	68
7	0.05	EtOAc	70	240	87
8	0.02	EtOH	70	90	68
9	0.04	EtOH	70	90	85
10	0.08	EtOH	70	90	95
11	0.05	EtOH	60	90	90
12	–	EtOH	70	90	N.R.

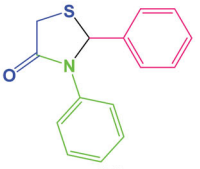
and the presence of 0.05 g of the catalyst was a suitable amount for accomplishment of the reaction. Furthermore, the more decrement of amount of the catalyst, decreased the efficiency of reaction. Also, as expected, no considerable effects was observed on the progress of yield in the reaction by enhancing the catalyst amount (Table 2, entries 8–10). Subsequently, the effect of temperatures was investigated in the model reaction, in which the highest yield of the product could be provided at the temperature of 70°C (Table 2, entries 11). Additionally, the effect of the solvents on the reaction was investigated (Table 2, entries 1–7), among which EtOH proved that could be selected as a most appropriate solvent for this reaction. Therefore, the best desired conditions for the synthesis of 1,3-thiazolidin-4-one derivatives can be obtained by using 0.05 g of the catalyst, EtOH solvent and a temperature of 70°C.

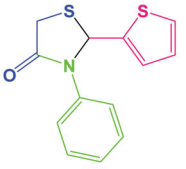
After the optimization of the conditions, the reaction of aromatic aldehyde (1.0 mmol), aryl amine (1.0 mmol), and thioglycolic acid (1.0 mmol), in the presence of 0.05 g of the catalyst, solvent (EtOH), and temperature of 70°C was studied. In this way, different aldehydes and amines with different electron-withdrawing and electron-donating groups were used, as exhibited in Table 3. In this work, it was demonstrated that the reaction could more proceed when an aldehyde with electron-withdrawing group and an amine with electron-donating group were employed. For investigation of the retrievability and reusability characteristic of catalyst, the model reaction was investigated in the presence of EtOH (5 mL) and 0.05 g of the catalyst at the temperature of 70°C. After completion of the reaction, the separated catalyst was washed several times with water and hot ethanol, followed by being placed in an oven to dry out. The catalyst recyclability is exhibited in Figure 2.

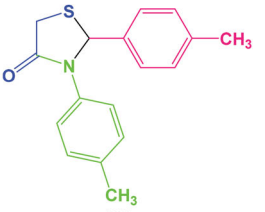
Since green chemistry aims to design products and processes of more environmentally friendliness along with less chemicals hazards, applying EtOH as a green solvent and utilization of a catalyst with well recyclability properties throughout the reactions are in line with the purpose of this work to comply with these rules.

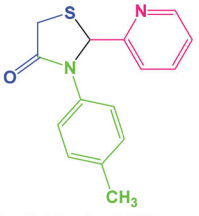
Table 3. Synthesis of 1,3-thiazolidin-4-one derivatives using the LDHs@PpPDA catalyst.

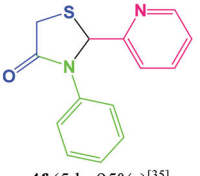

4a (2 h, 92%)[36]

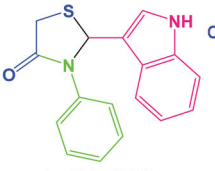

4b (4 h, 87%)[35]

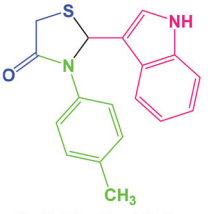

4c (6 h, 85%)[35]

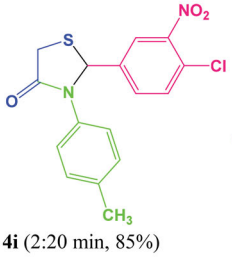

4d (2 h, 85%)[36]

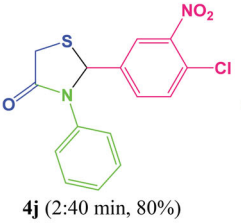

4e (1:30 min, 95%)

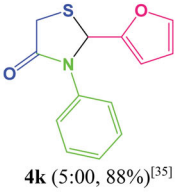

4f (5 h, 95%)[35]

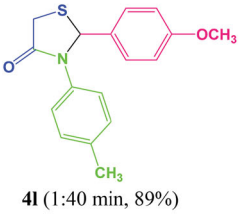

4g (2 h, 92%)

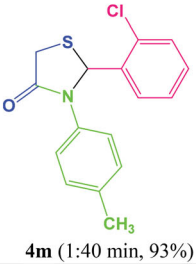

4h (1:50 min, 94%)

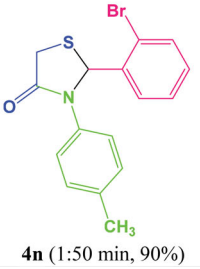

4i (2:20 min, 85%)


4j (2:40 min, 80%)


4k (5:00, 88%)[35]


4l (1:40 min, 89%)


4m (1:40 min, 93%)


4n (1:50 min, 90%)

The characterization of the catalyst was carried out by using different techniques including FT-IR spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and EELS maps [30]. In addition, the structure of the recovered catalyst was investigated prior and after the accomplishment of the reaction. LDHs@PpPDA was collected after the reaction and various analyses were conducted on them.

The FT-IR spectra of the catalyst before and after reaction are shown in Figure 3. As can be seen, the analogous characteristic bands of LDHs@PpPDA demonstrate the stability of the catalyst throughout the recycling process.

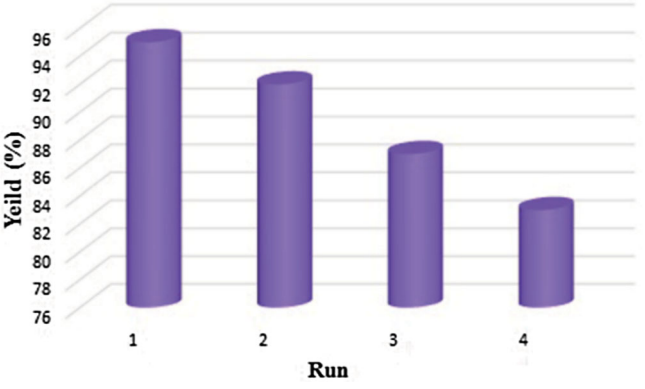


Figure 2. Recyclability of the LDHs@PpPDA.

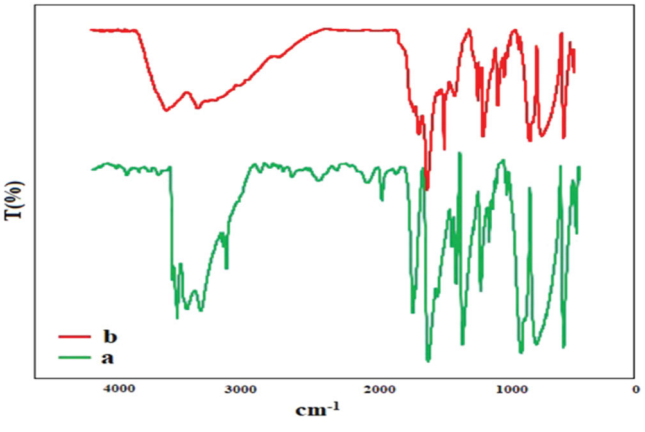


Figure 3. FT-IR spectra of LDHs@PpPDA before (a) and after (b) the reaction.

The EDX spectra of the catalyst before and after the reaction were almost identical, which indicated that there was no obvious changes for the catalyst composition after the reaction (Figure 4). In both spectra, the clear presence of N and C signals illustrate that the layered double hydroxides have been successfully coated with PpPDA.

SEM images of the catalyst before and after the reaction are exhibited in Figure 5. As shown, no significant alteration in the morphology of the catalyst was observed after the reaction, which definitely affirms the LDHs@PpPDA recyclability and stability under the reaction condition.

Figure 6 illustrates the X-ray diffraction patterns of the catalyst before and after the reaction. The positions and relative intensities of all characteristic diffractions at 2θ values of 10°, 30° and 40° indicated that the original structure and crystallinity of LDHs@PpPDA was successfully protected after the organic reaction.

Figure 7 shows FT-IR spectra for LDHs, PpPDA and LDHs@PpPDA. As shown, the characteristic peaks of LDHs and PpDA in 500–2000 cm^{-1} and 2500–4000 cm^{-1} were

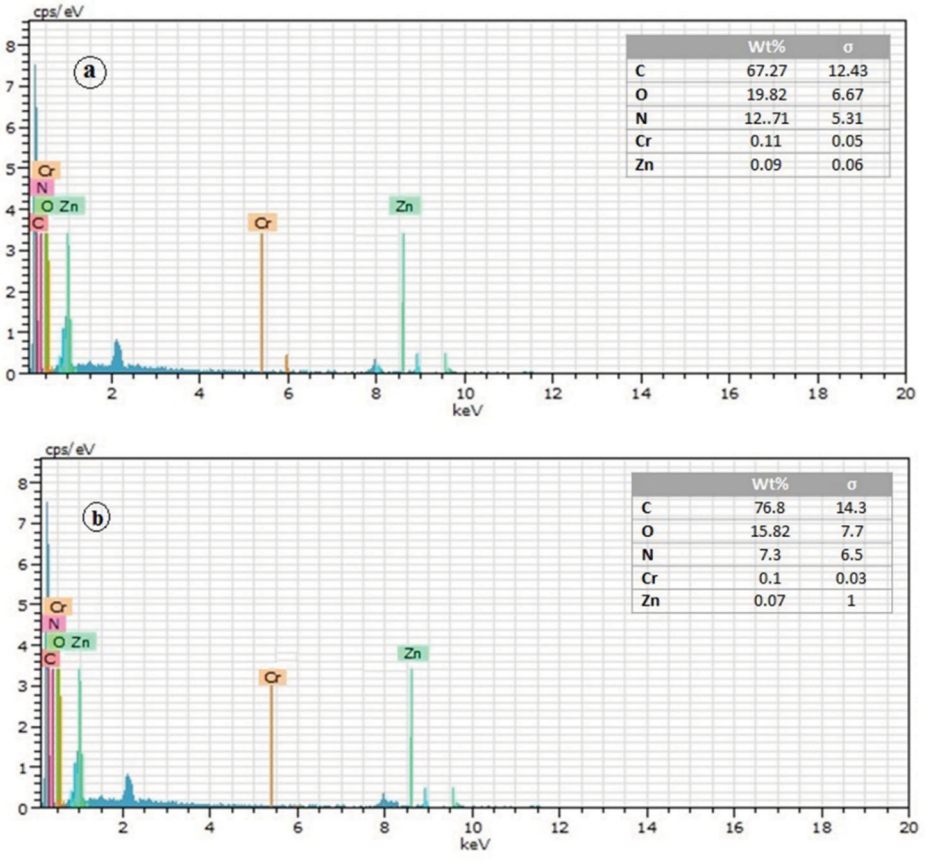


Figure 4. EDX spectra of LDHs@PpPDA before (a) and after (b) the reaction.

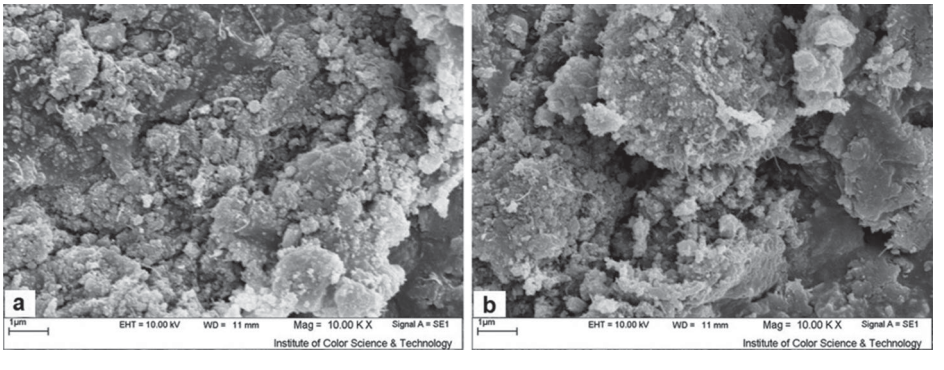


Figure 5. SEM images of LDHs@PpPDA before (a) and after (b) the reaction.

changed when LDHs coated with the polymer. These results confirm that PpPDA is coated on the surface of the LDHs.

A schematic illustration of a feasible mechanism for the synthesis of 1,3-thiazolidin-4-one derivatives by using LDHs@PpPDA catalyst, carried out through a three-component

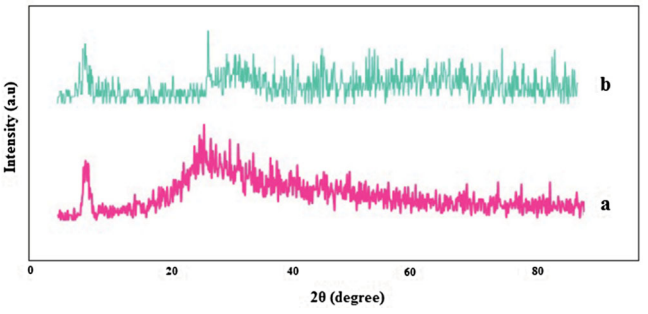


Figure 6. XRD pattern of LDHs@PpPDA before (a) and after (b) the reaction.

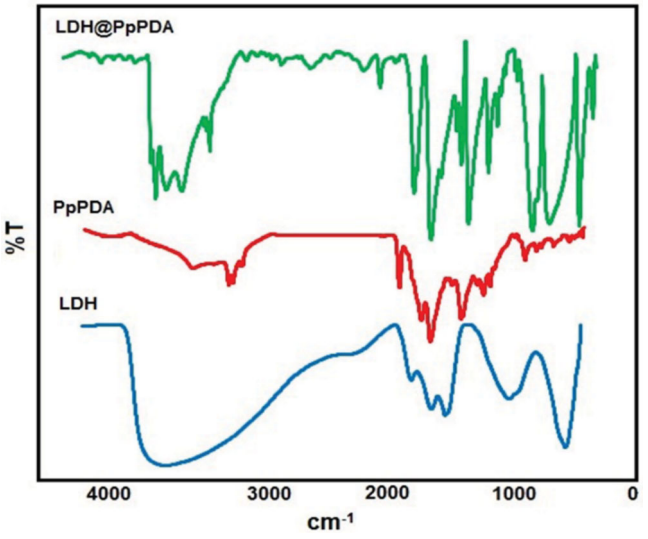
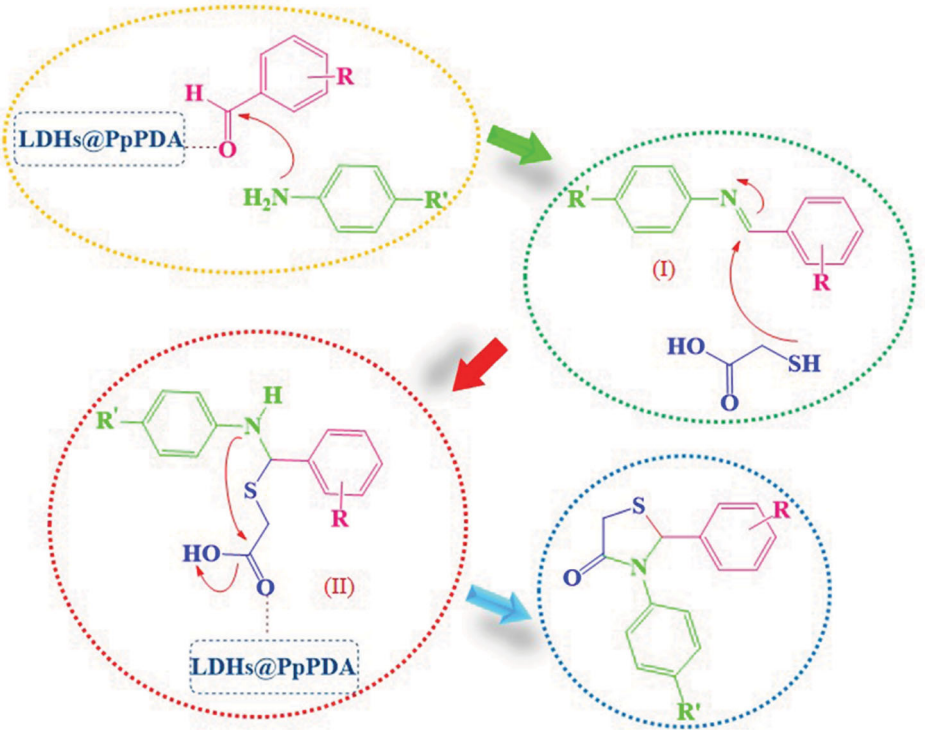


Figure 7. FT-IR spectra of LDH, PpPDA and LDHs@PpPDA.

reaction, is presented in Scheme 2. At the first step, in order to synthesize the intermediate (I), the condensation reaction between aldehyde and aryl amine is carried out by using LDHs@PpPDA, as the catalyst. In the next step, sulfur atom attacks as an electron-rich source to the imine bond and forms the intermediate (II). At the final step, intermediate (II) is activated by the catalyst and the product is produced by intramolecular cyclization.

3. Conclusion

A novel approach for the synthesis of 1,3-thiazolidin-4-one derivatives, as a high-importance class of heterocyclic compounds, has been reported in this research study. For this purpose, LDHs@PpPDA was employed as an outstanding and recyclable catalyst which can provide a significant catalytic activity in the preparation of 1,3-thiazolidin-4-one derivatives under various reaction conditions to follow the principles of green chemistry. By employing this process, numerous advantages including facile reaction work-up, superb



Scheme 2. Suggested reaction mechanism for the synthesis of 1,3-thiazolidin-4-one derivatives.

recyclability and reusability of the catalyst, short reaction time, considerable yield, and green mild reaction conditions could be obtained. The characterization of the newly prepared derivatives was carried out by using conventional spectroscopy techniques, and their structures were corroborated.

4. Experimental section

4.1. Chemicals and instruments

All commercial materials were supplied by Merck and Fluka Companies .^{1}H NMR and ^{13}C NMR spectra were analyzed by a spectrometer at 400 and 100 MHz, respectively, in DMSO-d_6. Fourier transform infrared (FT-IR) spectra were also analyzed by a Shimadzu 435-U-04 FT spectrophotometer from KBr pellets. A BUCHI 510 apparatus was utilized to measure melting points, carried out in open capillary tubes. Mass spectra were also analyzed by a Shimadzu QP 1100 BX mass spectrometer.

4.2. General procedure for preparation of LDHs@PpPDA catalyst

There are totally two major steps for the synthesis procedure of LDHs@PpPDA. First, layered double hydroxides (LDHs) were prepared through co-precipitation of solutions

containing Zn^{2+} and Cr^{3+} metal salts [33]. Then, the LDHs reacted with poly (*p*-phenylenediamine) to yield LDHs@PpPDA [30].

4.3. General procedure for synthesis of 1,3-thiazolidin-4-ones

In a 10-mL Round-bottom flask, a solution of an aromatic aldehyde (1.0 mmol), an aryl amine (1.0 mmol) and LDHs@PpPDA (0.05 g) in EtOH (5 mL) was stirred at 70°C for about 30 min. Afterward, thioglycolic acid (1.0 mmol) was added, and the mixture was stirred for appropriate times. TLC was employed to investigate the completion of the reaction. After that, when the reaction was accomplished, the reaction mixture was poured into a centrifuge tube in order to separate the catalyst by using centrifugation. The resulting solution was poured into a petri dish and the resulting precipitates were collected and washed with cold diethyl ether so that a highly pure product could be obtained. Physical and spectroscopic data (FT-IR, NMR, MS, and CHN) were employed to characterize pure crystals of 1,3-thiazolidin-4-ones.

4.4. Analytical data of products

2,3-diphenylthiazolidin-4-one (**4b**)

White powder. M.p. 129–130°C. Yield: 0.25 g (87%). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.6–7.63 (m, 11H), 3.31–3.61 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 25.59, 63.22, 124.6, 129.59, 134.66, 153.31, 156.8, 191.33.

3-phenyl-2-(thiophen-2-yl)thiazolidin-4-one (**4c**)

Cream powder. M.p. 148–149°C. Yield: 0.25 g (85%). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.56–7.97 (m, 8H), 5.67 (s, 1H), 3.37–3.68 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 17.88, 54, 09.51, 122.65, 125.83, 127.26, 129.04, 143.97, 146.79, 169.19.

2-(pyridin-2-yl)-3-(*p*-tolyl)thiazolidin-4-one (**4e**)

Cream powder. M.p. 158–162°C. Yield: 0.28 g (95%). FT-IR (KBr, ν, cm^{-1}): 2921, 1713, 1598, 1518, 1378, 1289, 790. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.5(s, 1H), 7.74 (s, 1H), 7.15-7.48 (m, 7H), 6.48 (s, 1H), 3.78 (m, 2H), 3.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.29, 32.12, 64.2, 120.64, 123.28, 124.52, 126.02, 128.69, 138.05, 149.25, 159.7, 170.87. Mass (*m/z*): 270. Anal. Calcd. For C15H14N2OS: C, 66.64; H, 5.22; N, 10.36. Found: C, 66.6; H, 5.24; N, 10.29.

2-(1*H*-indol-3-yl)-3-phenylthiazolidin-4-one (**4g**)

Red powder.. M.p. 168–169°C. Yield: 0.3 g (92%). FT-IR (KBr, ν, cm^{-1}): 3303, 2969, 1709, 1591, 1497, 1235, 743. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 15.46, 65.29, 112.06, 118.17, 121.61, 128.78, 135.95, 139.7, 175.53. Mass (*m/z*): 294. Anal. Calcd. For C17H14N2OS: C, 69.36; H, 4.79; N, 9.53. Found: C, 69.31; H, 4.82; N, 9.48.

2-(1*H*-indol-3-yl)-3-(*p*-tolyl)thiazolidin-4-one (**4h**)

Red powder. M.p. 171–174°C. Yield: 0.32 g (94%). FT-IR (KBr, ν, cm^{-1}): 3184, 1709, 1657, 1590, 1503, 1351, 1223, 745. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 11.15(s, 1H), 7.99–8.81 (m, 2H), 6.49–7.7 (m, 7H), 5.63 (s, 1H), 3.27 (m, 2H), 2.5 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 19.91, 33.87, 45.83, 110.68, 113.07, 119.21, 120.92, 129.46, 133.55, 137.3, 154.7, 170.75. Mass (*m/z*): 308. Anal. Calcd. For C18H16N2OS: C, 70.1; H, 5.23; N, 9.08. Found: C, 70.02; H, 5.28; N, 9.15.

2-(4-chloro-3-nitrophenyl)-3-(*p*-tolyl)thiazolidin-4-one (**4i**)

Yellow powder. M.p. 146–148°C. Yield: 0.32 g (85%). FT-IR (KBr, ν, cm^{-1}): 2922, 1714, 1605, 1518, 1350, 1134, 807. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7-8.77 (m, 7H), 6.78 (s, 1H), 3.41 (m, 2H), 2.5 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 20.23, 31.83, 68.7, 120.59, 129.82, 134.22, 139.34, 141.74, 150.59, 179.28. Mass (*m/z*): 348. Anal. Calcd. For C16H13ClN2O3S: C, 55.1; H, 3.76; N, 8.03. Found: C, 55.04; H, 3.85; N, 7.98.

2-(4-chloro-3-nitrophenyl)-3-phenylthiazolidin-4-one (**4j**)

Yellow powder. M.p. 153–155°C. Yield: 0.29 g (80%). FT-IR (KBr, ν, cm^{-1}): 2923, 1714, 1607, 1534, 1344, 1138, 735. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.87-8.35 (m, 8H), 6.61 (s, 1H), 3.49 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 30.13, 60.17, 123.99, 129.8, 133.55, 136.61, 139.01, 142.41, 147.24, 172.46. Mass (*m/z*): 334. Anal. Calcd. For $C_{15}H_{11}ClN_2O_3S$: C, 53.82; H, 3.31; N, 8.37. Found: C, 53.75; H, 3.37; N, 8.31.

2-(furan-2-yl)-3-phenylthiazolidin-4-one (**4k**)

Yellow powder. M.p. 138–140°C. Yield: 0.24 g (88%). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.26–7.79 (m, 8H), 5.79 (s, 1H), 3.29–379 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 30.62, 48.88, 112.92, 115.65, 117.59, 124.96, 127.66, 130.79, 143.98, 145.52, 188.62.

2-(4-methoxyphenyl)-3-(*p*-tolyl)thiazolidin-4-one (**4l**)

Yellow powder. M.p. 130–132°C. Yield: 0.29 g (89%). FT-IR (KBr, ν, cm^{-1}): 2960, 1672, 1591, 1496, 1438, 1393, 746. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.77-7.36 (m, 8H), 5.3 (s, 1H), 3.84 (m, 2H), 3.41 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 20.57, 31.15, 60.51, 71.77, 117.5, 125, 127.41, 130.13, 135.26, 138.32, 161.88, 172.47. Mass (*m/z*): 299. Anal. Calcd. For C17H17NO2S: C, 68.2; H, 5.72; N, 4.68. Found: C, 68.11; H, 5.79; N, 4.59.

2-(2-chlorophenyl)-3-(*p*-tolyl)thiazolidin-4-one (**4m**)

White powder. M.p. 128–131°C. Yield: 0.31 g (93%). FT-IR (KBr, ν, cm^{-1}): 2919, 1691, 1609, 1518, 1439, 807. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.87 (s, 1H), 6.73-7.48 (m, 7H), 6.5 (s, 1H), 3.32 (m, 2H), 2.5 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 19.79, 31.36, 69.41, 103.76, 114.74, 119.02, 120.14, 124.27, 129.47, 130.59, 135.43, 139.54, 178.71. Mass (*m/z*): 303. Anal. Calcd. For C16H14ClNOS: C, 63.26; H, 4.65; N, 4.61. Found: C, 63.18 H, 4.72; N, 4.54.

2-(2-bromophenyl)-3-(*p*-tolyl)thiazolidin-4-one (**4n**)

Cream powder. M.p. 136–138°C. Yield: 0.34 g (90%). FT-IR (KBr, ν, cm^{-1}): 2906, 1715, 1609, 1518, 1439, 807. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.47–7.59 (m, 2H), 6.31–7.04 (m, 6H), 5.76 (s, 1H), 3.25 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 19.9, 30.82, 67.34, 113.41, 117.52, 129.11, 132.86, 135.58, 139.02, 145.84, 148.24, 151.31, 178.95. Mass (*m/z*): 347. Anal. Calcd. For C16H14BrNOS: C, 55.18; H, 4.05; N, 4.02. Found: C, 55.09; H, 4.14; N, 3.98.

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Disclosure statement

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