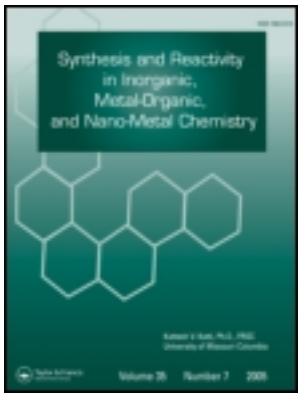

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Use of Sodium Molybdate Dihydrate as an Efficient Heterogeneous Catalyst for the Synthesis of Benzopyranopyrimidine Derivatives

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Sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) has been investigated as a heterogeneous catalyst for the one-pot pseudo–four-component synthesis of the benzopyranopyrimidine derivatives. This efficient and facile technique avoids the use of difficult workup and harsh reaction conditions.

Keywords benzopyranopyrimidine, multicomponent reaction, salicylaldehyde, sodium molybdate dihydrate

INTRODUCTION

In multicomponent reactions (MCRs), three or more reactants come together in a single reaction vessel to form new products that contain structural units of all the components. This type of reaction becomes increasingly important in organic and medicinal chemistry because it allows obtaining highly sophisticated poly functional molecules through simple one-pot procedures.[1–3] The chemistry of pyrimidines and their derivatives has been studied for over a century due to the association of these systems with a variety of biological properties. Benzopyranopyrimidines have been reported to possess significant pharmacological activities and several papers have focused on their synthesis and physiological activities.[4–6] Recently, a rapid progress has been done in the field of 4*H*-1-benzopyran-2-ones and related pyrimidine, due to the interaction of several drugs, receptor binding models, which enabled a systematic and rational design of novel inhibitors of various enzymes, such as HIV protease[7] and DNA gyrase or topoisomerase[8] tetrahydro-2H-benzopyran-2-ones. Though many synthetic strategies have been applied for preparation of fused pyrimidine derivatives, most of these methods suffer from some drawbacks, which include use of expensive or commercially non-available reagents, drastic reaction conditions, and longer time with difficult workup. Therefore, it has attracted continuous interest to develop methods for the synthesis of benzopyranopyrimidine compounds.

Sodium molybdate was first synthesized by the method of hydration. A more convenient synthesis is done by dissolving MoO_3 in sodium hydroxide at 50–70°C and crystallizing the filtered product.[9] The anhydrous salt is prepared by heating to 100°C.

$$MoO_3 + 2NaOH \rightarrow Na_2MoO_4.2H_2O \qquad [1]$$

The agriculture industry uses 1 million pounds sodium molybdate per year as a fertilizer.[10] In particular, its use has been suggested for treatment of whiptail in broccoli and cauliflower in molybdenum-deficient soils.[11] It is used in industry for corrosion inhibition, as it is a non-oxidizing anodic inhibitor.[9] The addition of sodium molybdate significantly reduces the nitrite requirement of fluids inhibited with nitrite-amine, and improves the corrosion protection of carboxylate salt fluids.[12] Moreover, sodium molybdate is used as an efficient heterogeneous catalyst for soybean oil methanolysis.[13] However, to the best of our knowledge; there are no reports about multicomponent reactions with $Na_2MoO_4.2H_2O$ as a catalyst. In continuation of our investigations of the synthesis of heterocyclic compounds and designing procedures in multicomponent reactions,[14] we have developed an efficient protocol for the synthesis of benzopyranopyrimidine derivatives, through the pseudo–four-component condensation of salicylaldehyde derivatives, malononitrile, and amines in the presence of $Na_2MoO_4.2H_2O$ as a catalyst, in ethanol at room temperature (Scheme 1).

EXPERIMENTAL

All the chemicals were purchased from Merck Company (Germany). Melting points were measured, using a capillary tube method with an electrothermal engineering LTD 9200 apparatus (United Kingdom). ^1H and ^{13}C NMR spectra were recorded on a Bruker AQS-AVANCE spectrometer (Germany)

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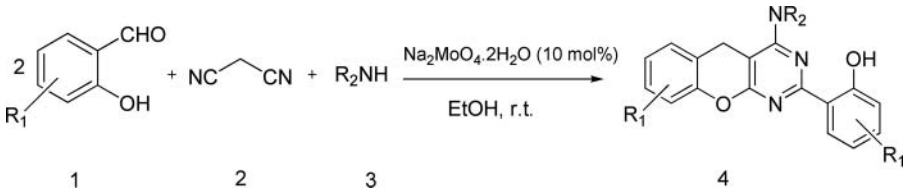


SCH. 1. Pseudo–four-component synthesis of benzopyranopyrimidine derivatives.

at 500 and 125 MHz, using TMS as an internal standard (DMSO solution). FTIR spectra were recorded using KBr disks on FT-IR Bruker Tensor 27 instrument (Germany). Mass spectra were documented on an Agilent Technology (HP) mass spectrometer (USA) operating at an ionization potential of 70 eV. Elemental analyses were performed using a Perkin-Elmer 2004 (II) CHN analyzer (USA).

Typical Procedure for the Synthesis of Compound 4a

A mixture of 2-hydroxybenzaldehyde (2 mmol), malononitrile (1 mmol), morpholine (1 mmol), and $Na_2MoO_4.2H_2O$ (10 mol%) in ethanol (10 mL) was stirred at room temperature for 10 h (the progress of the reaction was monitored by TLC). After completion, the reaction mixture was filtered and the precipitate washed with H_2O (3 × 5 mL) to afford pure **4a**. Catalyst is soluble in water and simply separated from the products.

Reusability of the $Na_2MoO_4.2H_2O$

One of the advantages of the heterogeneous catalysts is its ability to be recyclable. We were able to separate catalyst from the reaction medium easily by extraction with water. The catalyst was recovered by evaporation of the water of the aqueous layer in a vacuum oven. Then, the catalyst was dried under vacuum for 1 h, and reused in subsequent runs. In Table 1, the comparison of efficiency of the $Na_2MoO_4.2H_2O$ in synthesis of **4a** after four times is reported. As shown in Table 1, the first reaction using recovered $Na_2MoO_4.2H_2O$ afforded a similar yield to that obtained in the first run. In the second, third and fourth runs, the yields were gradually decreased.

Spectroscopic Data for the Some Products

For 2-(4-morpholino-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl)phenol (**4a**), IR (KBr): 3440, 3045, 2965, 1605 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 3.52 (t, 4H, $J = 4.3$ Hz, $2CH_2$), 3.80 (t, 4H, $J = 4.2$ Hz, $2CH_2$), 4.01 (s, 2H, CH_2), 6.91–6.94 (2 overlapped doublets, 2H, $J = 7.9$ and 7.8 Hz, ArH), 7.15–7.20 (m, 2H, ArH), 7.28 (t, 1H, $J = 7.2$ Hz, ArH), 7.35 (d, 1H, $J = 7.5$ Hz, ArH), 7.38–7.39 (dd, 1H, $J = 7.5$ and 1.6 Hz, ArH), 8.26 (d, 1H, $J = 7.8$ Hz, ArH), 13.09 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.56, 48.95, 66.86, 98.42, 116.95, 117.18, 118.93, 119.67, 120.70, 125.43, 128.98, 129.52, 129.89, 131.09, 150.60, 160.65, 161.41, 164.00, 164.86 ppm; MS (EI) m/z: 361(M^+); Anal. Calcd. for $C_{21}H_{19}N_3O_3$: C, 69.79; H, 5.30; N, 11.63. Found: C, 69.75; H, 5.45; N, 11.81.

TABLE 1
Reuseability of the $Na_2MoO_4.2H_2O$ for synthesis of 2-(4-morpholino-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl) phenol **4a**

Entry	Time (h)	Yield[a] (%)
1	12	85
2	13	70
3	15	60
4	20	55

[a]Isolated yield.

For 2-methoxy-6-(9-methoxy-4-morpholino-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl)phenol (**4d**), IR (KBr): 3445, 3035, 2945, 1600 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 3.51(brs, 4H, $2CH_2$), 3.76–3.80 (brs, 7H, $2CH_2$, OCH_3), 3.87 (s, 3H, OCH_3), 3.99 (s, 2H, CH_2), 6.83 (t, 1H, $J = 7.8$ Hz, ArH), 6.87 (d, 1H, $J = 7.5$ Hz, ArH), 6.98 (d, 1H, $J = 8.0$ Hz, ArH), 7.05–7.10 (m, 2H, ArH), 7.85 (d, 1H, $J = 8.0$ Hz, ArH), 13.30 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ: 25.65, 48.97, 56.60, 56.66, 66.85, 98.30, 111.71, 115.76, 118.78, 119.00, 120.95, 121.50, 125.26, 131.34, 139.89, 148.30, 149.41, 151.19, 161.67, 164.03, 164.75 ppm; MS (EI) m/z: 421(M^+); Anal. Calcd. for $C_{23}H_{23}N_3O_5$: C, 65.55; H, 5.50; N, 9.97. Found: C, 65.48; H, 5.55; N, 10.01.

For 2-methoxy-6-(9-methoxy-4-(piperidin-1-yl)-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl)phenol (**4e**), IR (KBr): 3420, 3045, 2930, 1605 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 1.69 (brs, 6H, $3CH_2$), 3.47 (brs, 4H, $2CH_2$), 3.80 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.96 (s, 2H, CH_2), 6.84 (t, 1H, $J = 7.9$ Hz, ArH), 6.88 (d, 1H, $J = 7.5$ Hz, ArH), 6.98 (d, 1H, $J = 8.0$ Hz, ArH), 7.05–7.10 (m, 2H, ArH), 7.85 (d, 1H, $J = 7.9$ Hz, ArH), 13.49 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 24.70, 25.78, 26.35, 49.65, 56.60, 56.66, 98.00, 111.68, 115.70, 118.70, 119.08, 120.91, 121.71, 125.18, 131.34, 140.05, 148.30, 149.41, 151.26, 161.65, 164.20, 165.01 ppm; MS (EI) m/z: 419(M^+); Anal. Calcd. for $C_{24}H_{25}N_3O_4$: C, 68.72; H, 6.01; N, 10.02. Found: C, 68.78; H, 6.15; N, 9.91.

For 2-(4-(dimethylamino)-9-methoxy-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl)-6-methoxyphenol (**4f**), IR (KBr): 3428, 3040, 2930, 1608 cm^{-1}; ^1H NMR (500 MHz, DMSO): δ 3.18 (s, 6H, $2CH_3$), 3.78 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.95 (s, 2H, CH_2), 6.81–6.87 (m, 2H, ArH), 6.98 (d, 1H, $J = 8.0$ Hz, ArH), 7.12–7.14 (m, 2H, ArH), 7.66 (d, 1H, $J = 7.9$ Hz, ArH), 13.39 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO): δ 24.72, 40.60,

56.63, 56.66, 98.05, 110.68, 114.79, 118.73, 119.18, 120.95, 121.78, 125.21, 129.49, 140.15, 148.33, 149.47, 151.27, 161.65, 164.22, 165.09 ppm; MS (EI) m/z: 379(M^+); Anal. Calcd. for $C_{21}H_{21}N_3O_4$: C, 66.48; H, 5.58; N, 11.08. Found: C, 66.48; H, 5.69; N, 10.99.

For 3-(8-hydroxy-4-(piperidin-1-yl)-5H-benzopyrano[2,3-*d*]pyrimidin-2-yl)benzene-1,2-diol (**4h**), IR (KBr): 3465, 3210, 3185, 2970, 1615 cm^{-1}; ^1H NMR (500 MHz, DMSO): δ 3.44 (brs, 4H, $2CH_2$), 3.80 (brs, 4H, $2CH_2$), 3.98 (s, 2H, CH_2), 6.72–6.75 (m, 2H, ArH), 6.79 (d, 1H, $J = 7.8$ Hz, ArH), 6.90 (d, 1H, $J = 7.5$ Hz, ArH), 6.94 (t, 1H, $J = 7.7$ Hz, ArH), 7.74 (d, 1H, $J = 7.9$ Hz, ArH), 8.94 (brs, 1H, OH), 9.80 (brs, 1H, OH), 13.26 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO): δ 25.53, 48.92, 66.81, 98.42, 113.85, 116.28, 117.98, 119.67, 121.79, 122.43, 125.98, 129.12, 141.89, 150.09, 153.60, 157.65, 161.81, 164.12, 164.80 ppm; MS (EI) m/z: 391(M^+); Anal. Calcd. for $C_{21}H_{19}N_3O_5$: C, 64.12; H, 4.87; N, 10.68. Found: C, 64.00; H, 4.95; N, 10.71.

For 4-(8-hydroxy-4-(piperidin-1-yl)-5H-benzopyrano[2,3-*d*]pyrimidin-2-yl)benzene-1,3-diol (**4i**), IR (KBr): 3460, 3215, 3185, 2965, 1615 cm^{-1}; ^1H NMR (500 MHz, DMSO): δ 3.46 (brs, 4H, $2CH_2$), 3.82 (brs, 4H, $2CH_2$), 4.01 (s, 2H, CH_2), 6.32 (d, 1H, $J = 7.9$ Hz, ArH), 6.56 (s, 1H, ArH), 6.77–6.80 (m, 2H, ArH), 7.13 (d, 1H, $J = 7.9$ Hz, ArH), 7.63 (d, 1H, $J = 8.0$ Hz, ArH), 8.94 (brs, 1H, OH), 9.85 (brs, 1H, OH), 13.31 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO): δ 25.50, 48.95, 66.86, 98.40, 116.85, 117.27, 118.94, 119.67, 120.82, 125.41, 129.01, 130.12, 130.76, 131.11, 150.63, 160.65, 161.81, 164.18, 164.82 ppm; MS (EI) m/z: 391(M^+); Anal. Calcd. for $C_{21}H_{19}N_3O_5$: C, 64.12; H, 4.87; N, 10.68. Found: C, 64.08; H, 5.01; N, 10.75.

RESULTS AND DISCUSSION

We herein report the use of $Na_2MoO_4.2H_2O$ catalyst for the one-pot pseudo–four-component synthesis of the benzopyranopyrimidine derivatives at room temperature with good yields. To choose the best reaction conditions, first a model reaction was selected, using 2 mmol salicylaldehyde with 1 mmol malononitrile and 1 mmol morpholine in the presence of catalytic amounts of $Na_2MoO_4.2H_2O$ at room temperature. We evaluated the amount of $Na_2MoO_4.2H_2O$ required for the model reaction. It was found that when increasing the amount of the $Na_2MoO_4.2H_2O$ from 5 to 7 and 10 mol%, the yields increased from 70 to 85 and 90, respectively. Using 10 mol% $Na_2MoO_4.2H_2O$ at room temperature is sufficient to push this reaction forward. More amounts of the catalyst did not improve the yields. In another investigation, the model reaction was examined in various solvents commonly used in organic synthetic procedures (Table 2). Polar solvent such as ethanol was much better than nonpolar solvents in terms of better yields and shorter reaction times, due to the better solubility of the reagents in polar solvent. In comparison with the recently reported method for preparation of benzopyranopyrimidine derivatives with $LiClO_4$ as a catalyst[15] and microwave-assisted reactions[16] our method gives a straightforward procedure and mild reaction conditions at room temperature with a new catalyst.

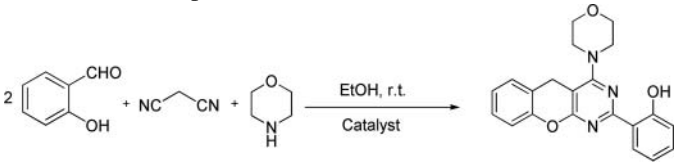
TABLE 2
Effect of solvent on the synthesis of 2-(4-morpholino-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl) phenol **4a**

Entry	Solvent	Time (h)	Yield (%)[a]
1	CH_3CN	24	55
2	CH_2Cl_2	24	10
3	Toluene	48	Very low
4	C_2H_5OH	10	90

[a]Yields refer to isolated pure products.

In order to achieve suitable conditions for the synthesis of the benzopyranopyrimidines **4**, several classes of heterogeneous catalysts have been investigated. Heterogeneous catalysts are advantageous because they are usually recyclable and products purification is greatly facilitated. Catalysts based on molybdenum compounds showed high efficiency in multicomponent reactions.[17,18] We studied this reaction with heteropolyacids including Mo, such as $H_3[PMo_{12}O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_{14}[NaP_5W_{29}MoO_{110}]$, MoO_3, and $Na_2MoO_4.2H_2O$. The Brønsted acids such as $H_3[PMo_{12}O_{40}]$, $H_6[PMo_9V_3O_{40}]$ and $H_{14}[NaP_5W_{29}MoO_{110}]$ promoted the reaction in 30–65% yields. (Table 3, entries 2–4). Under the same conditions, MoO_3 gave benzopyranopyrimidine **4a** in 45% yield after 13 h (Table 3, entry 5). The best overall yield was obtained using 10 mol% $Na_2MoO_4.2H_2O$ in ethanol at room temperature (Table 3, entry 1).

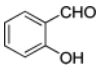
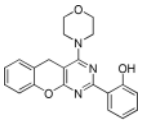
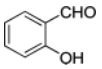
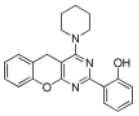
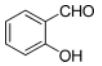
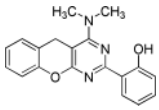
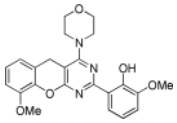
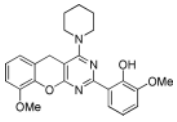
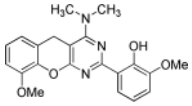
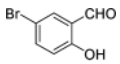
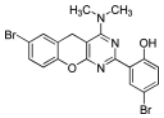
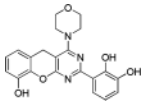
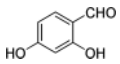
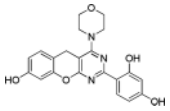
TABLE 3
Effect of catalyst on the pseudo–four-component synthesis of 2-(4-morpholino-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl) phenol **4a**



Entry	Catalyst	Time (h)	Yield[a] (%)
1	$Na_2MoO_4.2H_2O$ (10 mol%)	10	90
2	$H_3[PMo_{12}O_{40}]$ (10 mol%)	15	30
3	$H_6[PMo_9V_3O_{40}]$ (10 mol%)	13	40
4	$H_{14}[NaP_5W_{29}MoO_{110}]$ (10 mol%)	10	65
5	MoO_3 (10 mol%)	13	45

[a]The yields refer to isolated products.

TABLE 4
Synthesis of benzopyrano[2,3-*d*]pyrimidine derivatives **4**[a]

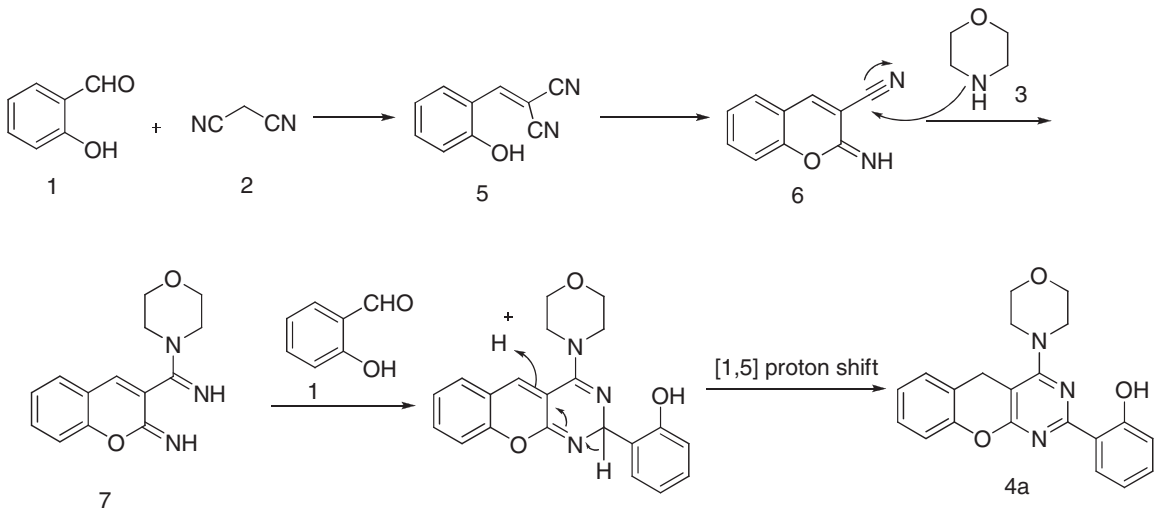
Entry	Aldehyde	Amine	Product[b]	Time (h)	Mp (°C) Found (Lit.)	Yield[c] (%)
4a				10	200–204 210[16]	90
4b				11	178–180 187[16]	80
4c				12	174–176 177–179[15]	70
4d				8	217–219 231[16]	90
4e				8.30	193–196 181–183[15]	80
4f				10	201–204 —	75
4g				18	195–198 196–198[15]	60
4h				8	171–173 —	75
4i				10	175–177 —	70

[a]All reactions were carried out using 2 mmol of 2-hydroxybenzaldehyde derivatives, 1 mmol malononitrile and 1 mmol amine in the presence of $Na_2MoO_4.2H_2O$ as a catalyst, in ethanol at room temperature.

[b]All products were characterized by IR, ^1H and ^{13}C NMR, mass spectroscopy, and CHN.

[c]The yields refer to isolated products.

As shown in Table 4, to establish the generality of the method, a wide variety of suitable substrates were employed. Various salicylaldehydes and amines were used and the reactions afforded the corresponding products. Salicylaldehydes bearing different substitutes, such as OMe, Br, and OH on the aryl rings were suitable to the reaction. In the investigation of various salicylaldehydes, it was found that electron-donating substituents such as OMe and OH are the most active in the reaction. However, electron-withdrawing groups such as Br result in a low amount of yield with long reaction time. All structures were fully characterized by FTIR, ^1H, ^{13}C NMR, mass, and CHN. The treatment of 2 mmol 2-hydroxybenzaldehyde with 1 mmol morpholine and 1 mmol malononitrile in ethanol in the presence of catalyst afforded 2-(4-morpholino-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl) phenol **4a**. For instance, the IR spectrum of compound **4a** showed absorption band at region 3440 cm^{-1} (OH). In ^{1}HNMR



SCH. 2. Investigation of a possible reaction mechanism for 2-(4-morpholino-5*H*-benzopyrano[2,3-*d*]pyrimidin-2-yl) phenol **4a.**

spectrum, the resonance signal of the OH group was shifted to the most downfield region (13.09 ppm) due to the strong intermolecular hydrogen bonding. This spectrum also exhibited two triplets at 3.52 and 3.80 ppm arising from methylene protons of the morpholine and a singlet at 4.01 ppm for aliphatic methylen protons of pyran. Also the area of integration for the aromatic protons is in accordance with the assignment. The ^{13}C NMR spectrum of **4a** showed 19 distinct resonances in agreement with the suggested structure. Although Bazgir et al.[15] reported that achieving the ^{13}C NMR data for some compounds was not possible because of the poor solubility of the synthesized compound in DMSO (for example compound **4e**), all prepared compounds including **4e** showed good solubility in DMSO and subsequently ^{13}C NMR data were obtained.

The formation of product **4a** can be explained by Knoevenagel condensation, Pinner reaction, and proton shift as shown in Scheme 2. The process represents a typical cascade reaction in which the salicylaldehyde **1** condenses with malononitrile **2** to afford derivative **5** followed by subsequent Pinner reaction to give intermediate **6**. After the condensation malononitrile **2** and salicylaldehyde **1** to produce intermediate **6**, intermediate **6** is attacked via morpholine **3** to give the intermediate **7**. Finally, intermediate **7** reacts with another molecule of salicylaldehyde **1** followed by [1,5] proton shift to form the desired product **4a** (Scheme 2).

CONCLUSION

In summary, we have developed benzopyranpyrimidine compounds synthesis under relatively mild conditions in the presence of a catalytic amount of $Na_2MoO_4.2H_2O$ in ethanol. The low toxicity of the catalyst, simple experimental procedure, heterogeneous catalyst, and good yields of the products are the advantages.

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