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# One-pot, three-component synthesis of pyranocoumarins containing an aroyl group

**Abstract:** An expeditious method to prepare pyranocoumarins containing an aroyl group by the three-component reaction of 4-hydroxycoumarin with arylglyoxals and malononitrile is described. The reaction is efficiently catalyzed by Mohr's salt, and the products were obtained in good to excellent yields with high purity. The method is simple, inexpensive, and environmentally friendly.

**Keywords:** arylglyoxal; catalyst; 4-hydroxycoumarin; malononitrile; Mohr's salt; pyranocoumarins.

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## Introduction

Pyran, a well-known heterocyclic system, is a common and important moiety of a variety of natural products and medicinal agents [1, 2]. Besides, pyrano-fused heterocycles have attracted considerable synthetic interest because of their biological, pharmaceutical, and material properties [3–5]. In the last decades, some research groups have focused on pyranocoumarins and their heteroanalogous chemistry because they exhibit a variety of biological properties such as antifungal, insecticidal, anticancer, anti-HIV, anti-inflammatory, and antibacterial activities [6–8]. Among pyranocoumarins, the pyrano[3,2-*c*]coumarin compounds are the most synthetically accessible. Thus far, several methods have been developed for the preparation of pyrano[3,2-*c*]coumarins, but the most conventional approach to this class of compounds is the three-component condensation of a 4-hydroxycoumarin, an aromatic aldehyde, and

malononitrile in the presence of weakly basic or acidic catalysts [9–13]. To the best of our knowledge, there is no report on the synthesis of pyrano[3,2-*c*]coumarins starting from arylglyoxals in a three-component reaction.

In recent years, we have been involved in the synthesis of new heterocycles containing a coumarin moiety [14–18]. Herein, we wish to report the synthesis of new pyrano[3,2-*c*]coumarins **4** by the one-pot, three-component reaction of 4-hydroxycoumarin (**1**) with arylglyoxals **2** and malononitrile (**3**) in good to excellent yields using Mohr's salt as an efficient catalyst. Considering that there are many reports on the synthesis of pyranocoumarins employing aromatic aldehydes, in this report, some arylglyoxals are introduced as potential alternatives to produce molecules of type **4**-containing aroyl groups.

## Results and discussion

On the basis of our previous experience related to the synthesis of pyranocoumarins [19], the model reaction initially involved the solvent system EtOH/H<sub>2</sub>O (1:1). After some optimizations including temperature and catalyst amounts, it was found that generally good yields of compound **4a** were obtained when the mixture of the three starting components with Mohr's salt (10 mol%) was initially stirred in EtOH/H<sub>2</sub>O (1:1) at room temperature and then heated under reflux (Scheme 1). During the optimization of the reaction conditions, it was found that the Mohr's salt is a more effective catalyst than common bases and acids. Table 1 shows the results obtained with other attempted catalysts in the synthesis of **4a**.

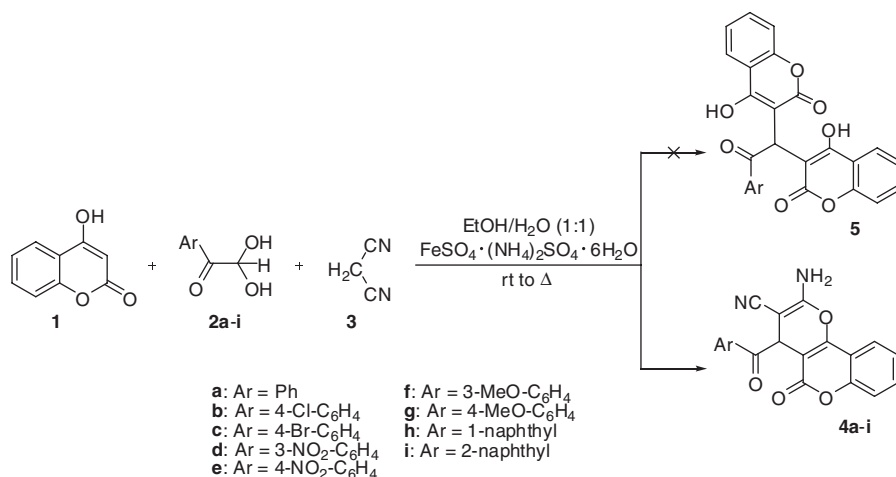
The results illustrate the merit of Mohr's salt in comparison with other catalysts in the aspects of yields. No product was obtained in the attempted reactions of entries 1–4 (Table 1). Product **4a** was obtained in low yield in the presence of NH<sub>4</sub>Cl (entry 5). The scope of this reaction was studied using a range of arylglyoxals **2**. In all cases, derivatives of type **4** with high purity were obtained. It was also observed that the process tolerates both electron-donating and electron-withdrawing substituents on the aromatic ring. The reactions were completed after 100–150 min, and the products were separated by simple filtration of the precipitate. There was no evidence of the

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**Scheme 1** Synthesis of pyrano[3,2-c]coumarins.

**Table 1** Comparison of Mohr's salt with other catalysts in the synthesis of **4a**.

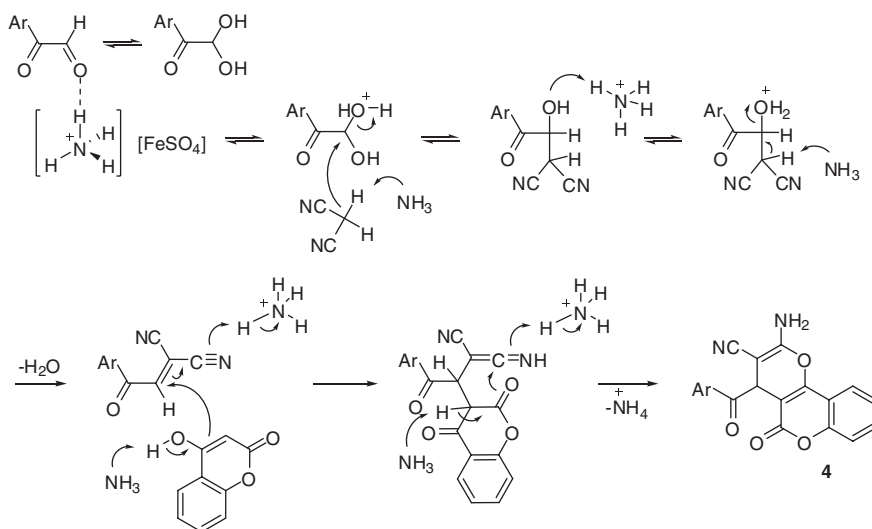
Entry	Catalyst	Yield (%)	Time (min)
1	FeCl <sub>3</sub>	—	240
2	AlCl <sub>3</sub>	—	240
3	<i>p</i> -TSA	—	240
4	Na <sub>2</sub> CO <sub>3</sub>	—	240
5	NH <sub>4</sub> Cl	43	240
6	Mohr's salt	80	100

presumed compound **5** (Scheme 1) that would be derived by the reaction of two equivalents of 4-hydroxycoumarin with the aroyl glyoxal.

The structures of compounds **4** were assigned on the basis of comprehensive spectroscopic and elemental

analyses. For example, the <sup>1</sup>H NMR spectrum of **4a** exhibits two sharp singlets for methine (δ=5.42) and NH<sub>2</sub> (δ=7.69) protons. The signals at δ=7.53–8.16 correspond to aromatic protons. The proton decoupled <sup>13</sup>C NMR spectrum of **4a** shows 18 distinct resonances in agreement with the proposed structure. Characteristic signals at δ=198.1, 51.9, and 37.1 correspond to ketonic C=O, olefinic carbon, and carbon joined to nitrile group, respectively [20]. The IR spectrum of **4a** shows characteristic bands at 3402–3292 cm<sup>-1</sup> (NH<sub>2</sub>), 2201 cm<sup>-1</sup> (CN), 1708 cm<sup>-1</sup> (lactonic C=O), and 1678 cm<sup>-1</sup> (ketonic C=O).

The suggested mechanisms for the formation of **4** is shown in Scheme 2. The reaction is thought to take place in three steps. The initial event involves the generation of an intermediate aroylmethylene via the condensation of the aroyl glyoxal and malononitrile. In the next step, a



**Scheme 2** A plausible mechanism for the synthesis of **4** using Mohr's salt.

Michael-type addition and subsequent intramolecular heterocyclization give the desired product **4**.

## Conclusion

Synthesis of new pyrano[3,2-*c*]coumarins via the three-component coupling reaction of 4-hydroxycoumarin with arylglyoxals and malononitrile is described. The advantages of the present method are high yields, short reaction times, excellent chemoselectivity, use of commercial Mohr's salt as an extremely efficient catalyst, and ease of product isolation and purification.

## Experimental

Chemicals were purchased from Merck and Aldrich chemical companies. Aryl glyoxals were synthesized according to our previous reports [21, 22]. Melting points were measured on an electrothermal KSB1N apparatus. IR spectra were recorded by a JASCO FT-IR-680 plus spectrometer using KBr pellets.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on an FT-NMR Bruker Avance spectrometer at 300 and 75 MHz, respectively, in  $\text{DMSO}-d_6$ . TLC was performed on TLC-grade silica gel-G/UV 254-nm plates.

### General procedure for the synthesis of compounds **4**

To a 25-mL round-bottomed flask, 4-hydroxycoumarin (1.0 mmol), arylglyoxal (1.2 mmol), malononitrile (1.2 mmol),  $\text{EtOH}/\text{H}_2\text{O}$  (1:1, 10 mL), and Mohr's salt (0.1 mmol) were added. The mixture was stirred at room temperature for 30 min, then vigorously stirred and heated under reflux for the period indicated below. The progress of the reaction was monitored by TLC. Upon completion, the reaction system was cooled to room temperature, and the precipitate was filtered. The pure product was obtained after crystallization from  $\text{EtOH}/\text{THF}$  (3:1).

**2-Amino-4-benzoyl-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4a**)** Light yellow crystals; yield 80%; mp 272–274°C; time 100 min; IR:  $\nu$  3402, 3292, 2201, 1708, 1678, 1606, 1373, 1064  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.16 (s, 2H,  $J = 8$  Hz), 7.90 (dd, 1H,  $J_1 = 8$ ,  $J_2 = 1.6$  Hz), 7.79 (dd, 1H,  $J_1 = 8$  Hz,  $J_2 = 1.6$  Hz), 7.69 (s, 2H), 7.62 (t, 2H,  $J = 8$  Hz), 7.57–7.53 (m, 2H), 5.42 (s, 1H);  $^{13}\text{C}$  NMR:  $\delta$  198.1, 160.0, 159.5, 154.7, 152.1, 135.3, 134.1, 133.3, 129.1, 128.8, 125.0, 122.1, 118.5, 116.8, 112.5, 101.9, 51.9, 37.1. Anal. Calcd for  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 69.76; H, 3.51; N, 8.14. Found: C, 69.55; H, 3.41; N, 8.09.

**2-Amino-4-(4-chlorobenzoyl)-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4b**)** Light yellow crystals; yield 90%; mp 263–265°C; time 120 min; IR:  $\nu$  3319, 3186, 3027, 2871, 2205, 1713, 1673, 1587, 1375, 1058, 759  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.20 (d, 2H,  $J = 8$  Hz), 7.89 (dd, 1H,  $J_1 = 8$  Hz,  $J_2 = 1.4$  Hz), 7.81–7.69 (m, 5H), 7.57–7.52 (m, 2H), 5.43 (s, 1H);  $^{13}\text{C}$  NMR:  $\delta$  197.2, 160.0, 159.5, 154.7, 152.1, 139.2, 134.1, 133.3, 130.9, 129.0, 125.0, 122.1, 118.4, 116.8, 112.5, 101.6, 51.7, 37.2. Anal. Calcd for  $\text{C}_{20}\text{H}_{11}\text{ClN}_2\text{O}_4$ : C, 63.42; H, 2.93; N, 7.40. Found: C, 63.61; H, 2.99; N, 7.35.

**2-Amino-4-(4-bromobenzoyl)-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4c**)** Light yellow crystals; yield 85%; mp 263–265°C; time 140 min; IR:  $\nu$  3316, 3186, 3027, 2871, 2203, 1715, 1673, 1582, 1374, 1057, 620  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.10 (d, 2H,  $J = 8.6$  Hz), (dd, 1H,  $J_1 = 8$  Hz,  $J_2 = 1.6$  Hz), 7.85 (d, 2H,  $J = 8$  Hz), 7.75 (td, 1H,  $J_1 = 8$  Hz,  $J_2 = 1.6$  Hz), 7.71 (s, 2H), 7.58–7.53 (m, 2H), 5.42 (s, 1H);  $^{13}\text{C}$  NMR: 197.5, 159.5, 154.7, 152.1, 134.4, 133.4, 132.0, 131.0, 125.0, 122.1, 116.8, 112.5, 101.6, 51.7, 37.2. Anal. Calcd for  $\text{C}_{20}\text{H}_{11}\text{BrN}_2\text{O}_4$ : C, 56.76; H, 2.62; N, 6.62. Found: C, 56.89; H, 2.51; N, 6.58.

**2-Amino-4-(3-nitrobenzoyl)-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4d**)** Yellow crystals; yield: 85%; mp 248–250°C; time 110 min; IR:  $\nu$  3415, 3086, 2928, 2197, 1712, 1673, 1609, 1525, 1385, 1352, 1063  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.83 (t, 1H,  $J = 1.8$  Hz), 8.65 (d, 1H,  $J = 8$  Hz), 8.59 (d, 1H), 7.97 (d, 1H,  $J = 8$  Hz), 7.93–7.89 (m, 1H), 7.82–7.77 (m, 3H), 7.59–7.53 (m, 2H), 5.57 (s, 1H) ppm;  $^{13}\text{C}$  NMR:  $\delta$  197.0, 160.1, 159.5, 154.8, 152.1, 148.1, 136.6, 135.2, 133.5, 130.9, 128.3, 125.1, 123.1, 122.2, 118.5, 116.8, 112.5, 101.3, 51.2, 37.6. Anal. Calcd for  $\text{C}_{20}\text{H}_{11}\text{N}_3\text{O}_6$ : C, 61.70; H, 2.85; N, 10.79. Found: C, 61.88; H, 2.77; N, 10.83.

**2-Amino-4-(4-nitrobenzoyl)-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4e**)** Yellow crystals; yield 85%; mp 273–275°C; time 105 min; IR:  $\nu$  3461, 3336, 2192, 1720, 1681, 1613, 1517, 1383, 1326, 1070, 1064  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.44 (d, 2H,  $J = 8$  Hz), 8.40 (d, 2H,  $J = 8$  Hz), 7.90 (dd, 1H,  $J_1 = 8$  Hz,  $J_2 = 1.4$  Hz), 7.79 (td, 3H,  $J_1 = 8$ ,  $J_2 = 1.5$  Hz), 7.59–7.54 (m, 2H), 5.51 (s, 1H);  $^{13}\text{C}$  NMR:  $\delta$  197.7, 160.1, 159.5, 154.8, 152.1, 150.4, 140.2, 133.5, 130.4, 125.1, 124.0, 122.2, 116.8, 112.5, 101.3, 51.2, 37.9. Anal. Calcd for  $\text{C}_{20}\text{H}_{11}\text{N}_3\text{O}_6$ : C, 61.70; H, 2.85; N, 10.79. Found: C, 61.79; H, 2.72; N, 10.71.

**2-Amino-4-(3-methoxybenzoyl)-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4f**)** Light yellow crystals; yield 90%; mp 268–270°C; time 100 min; IR:  $\nu$  = 3477, 3344, 3072, 2934, 2196, 1721, 1674, 1577, 1386, 1065  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  7.90 (dd, 1H,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz), 7.78 (td, 2H,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz), 7.70 (s, 2H), 7.62 (t, 1H,  $J = 2$  Hz), 7.57–7.52 (m, 3H), 7.32 (dd, 1H,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz), 5.40 (s, 1H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR:  $\delta$  197.7, 160.0, 159.6, 159.4, 154.7, 152.1, 136.6, 133.3, 130.0, 125.0, 122.1, 121.6, 120.2, 118.5, 116.8, 113.5, 112.6, 101.9, 55.3, 52.0, 37.4. Anal. Calcd for  $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_5$ : C, 67.38; H, 3.77; N, 7.48. Found: C, 67.48; H, 3.70; N, 7.56.

**2-Amino-4-(4-methoxybenzoyl)-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4g**)** Light yellow crystals; yield 80%; mp 266–268°C; time 130 min; IR:  $\nu$  = 3426, 3320, 2926, 2200, 1714, 1673, 1597, 1383, 1062  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.15 (d, 2H,  $J = 9$  Hz), 7.89 (dd, 1H,  $J_1 = 8$  Hz,  $J_2 = 1.4$  Hz), 7.80–7.74 (td, 1H,  $J_1 = 8$  Hz,  $J_2 = 1.6$  Hz), 7.65 (s, 2H), 7.56 (d, 1H,  $J = 9$  Hz), 7.53 (d, 1H,  $J = 9$  Hz), 7.14 (d, 2H,  $J = 9.0$  Hz), 5.36 (s, 1H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR:  $\delta$  196.2, 163.9, 160.0, 159.5, 154.6, 152.0, 133.2, 131.6, 128.1, 124.9, 122.1, 118.6, 116.7, 114.1, 112.6, 102.1, 55.6, 52.2, 36.7. Anal. Calcd for  $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_5$ : C, 67.38; H, 3.77; N, 7.48. Found: C, 67.40; H, 3.73; N, 7.40.

**2-Amino-4-(1-naphthoyl)-3-cyano-4*H*,5*H*-pyrano[3,2-*c*]chromene-5-one (**4h**)** Yellow crystals; yield 90%; mp 271–273°C; time 100 min; IR:  $\nu$  3477, 3327, 3050, 2923, 2191, 1727.91, 1674.87, 1573.63, 1381.75, 1177  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.37 (m, 2H), 8.24 (d, 1H,  $J = 8$  Hz), 8.09–8.05 (m, 1H), 7.92 (dd, 1H,  $J = 8$  Hz,  $J_2 = 1.8$  Hz), 7.80 (td, 1H,  $J = 8$  Hz,  $J_2 = 1.6$  Hz), 7.75–7.70 (m, 3H), 7.66–7.54 (m, 4H), 5.43 (s, 1H);  $^{13}\text{C}$  NMR:  $\delta$  200.3, 160.2, 159.6, 154.6, 152.2, 134.2, 133.4, 133.3, 133.2, 129.8, 129.0, 128.5, 128.0, 126.5, 125.1, 125.0, 124.7, 122.2, 118.3,

116.8, 112.6, 101.7, 51.4, 38.6. Anal. Calcd for  $C_{24}H_{14}N_2O_4$ : C, 73.09; H, 3.58; N, 7.10. Found: C, 73.13; H, 3.55; N, 7.01.

**2-Amino-4-(2-naphthoyl)-3-cyano-4H,5H-pyrano[3,2-c]chromene-5-one (4i)** Yellow crystals; yield 95%; mp 278–280°C; time 100 min; IR:  $\nu$  3428, 3321, 2938, 2199, 1714, 1674, 1631, 1597, 1569, 1382, 1172  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.44 (s, 1H), 7.97 (d, 1H,  $J = 8$  Hz), 7.83 (d, 1H,  $J = 8$  Hz), 7.74 (t, 1H,  $J = 8$  Hz), 7.62–7.52 (m, 3H), 7.48 (d, 1H,  $J = 8$  Hz), 7.44 (t, 1H,  $J = 8$  Hz), 7.39 (s, 2H), 7.33 (d, 1H,  $J = 7$  Hz), 5.47 (s, 1H);  $^{13}\text{C}$  NMR:  $\delta$  199.6, 159.5, 157.8, 153.8, 152.0, 133.2, 132.9, 130.9, 128.4, 127.4, 126.1, 126.0, 125.8, 125.7, 124.7, 123.4, 122.4, 119.1, 116.6, 112.9, 104.6, 53.6, 37.2. Anal. Calcd for  $C_{24}H_{14}N_2O_4$ : C, 73.09; H, 3.58; N, 7.10. Found: C, 73.17; H, 3.60; N, 7.04.

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