POTASSIUM 2-OXOIMIDAZOLIDINE-1,3-DIIDE AS A NOVEL CATALYST FOR GRIND SYNTHESIS OF PYRANO[4,3-*b*]CHROMENONE

MOHAMMAD NIKPASSAND,[*, a] *LEILA ZARE FEKRI,*[b] *ZAHRA GHARIB,*[a] *ZEINAB JAFARIAN*[a]

[a]*Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran*
[b]*Department of Chemistry, Payame Noor University, PO Box 19395-3697 Tehran, Iran*

ABSTRACT

A novel, clean, mild and eco-friendly benign route to pyrano[4,3-*b*]chromenes through cyclocondensation reaction of *β*-naphthol, aldehydes and 4-hydroxycoumarin, using POImD as a novel and reusable organometallic catalyst, is described. The present methodology offers several advantages such as simple work-up procedure, short reaction time, high yields of product with better purity and green aspect by avoiding toxic catalyst and hazardous solvent. All of synthesized compounds were characterized by IR, NMR and elemental analyses.

Keywords: Potassium 2-oxoimidazolidine-1,3-diide, pyrano[4,3-*b*]chromenes, 4-hydroxycoumarin, *β*-naphthol.

INTRODUCTION

Chromenes and their derivatives have attracted considerable interest because of wide range of biological properties [1, 2]. A number of this class of compounds can act as anti-alzheimer[3], anti-tumor[4], anti-bacterial [5,6], anti-cancer [7], anti-coagulant [7], diuretic [8], anti-malaria [9], and spasmolytic agents [10].

Based on the importance of these compounds, a number of research groups have developed methodologies to synthesize these compounds. The approaches used include intramolecular cyclization of Wittig intermediates [11], Baylis–Hillman reaction of salicylaldehydes with methyl vinyl ketones [12], aldol condensation of *N*-(Un)substituted quinolone-3-carbaldehydes and (Un)substituted benzofuran-3(2*H*)-ones [13], electrocyclic ring closure of vinylquinones [14], reductive desulfurization via Prins cyclization [15], ring-closing olefin metathesis [16], catalytic Petasis reaction of salicylaldehydes [17], Pd-catalyzed ring closure of 2-isoprenyl phenols [18], microwave-assisted reaction of 2-hydroxybenzaldehyde with enamines [19], Claisen rearrangement of propargyl phenol ethers [20], and the ylide annulation reaction [21].

However, most of these reported methods suffer from environmental pollution, exotic reaction conditions, tedious preparation procedure, long reaction time, expensive reagents or catalysts, unsatisfactory yields and complicated operations. In order to make this reaction simple and green, herein, we used POImD to synthesis of pyrano[4,3-*b*]chromenes by the three-component reaction of *β*-naphthol, hydroxycoumarin and various arylaldehydes at room temperature in aqua media.

Water has a unique media in chemistry and is one of the best solvents, owing to its features such as being eco-friendly, clean, green, nontoxic, non-flammable, safe, low-cost and readily available in organic transformations. Also, the use of aqua media not only diminishes the risk entailed in the use of organic solvents but also improves the rate of many chemical reactions [22-24].

EXPERIMENTAL

Materials and measurements

Chemicals were purchased from Merck and Fluka. All solvents used were dried and distilled according to standard procedures. Thin Layer Chromatography (TLC) was done with TLC Silica gel 60; Aluminum sheet from Merck. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were determined on a Shimadzu FT-IR 8600 spectrophotometer. ^{1}H and ^{13}C NMR spectra were determined on a Bruker 400 DRX Avance instrument at 500 and 125 MHz. Elemental analyses were done on a Carlo-Erba EA1110CNNO-S analyzer and agreed with the calculated values.

General procedure for the synthesis of potassium 2-oxoimidazolidine-1,3-diide (POImD)

A mixture of imidazolidin-2-one (20 mmol), KOH (20 mmol) and H_2O (10 mL) was stirred overnight. Following the completion of the reaction, as indicated by TLC, potassium 2-oxoimidazolidine-1,3-diide (POImD) was separated from the reaction mixture by filtration. POImD was purified by recrystallization from EtOH to afford pure products.

General procedure for the synthesis of pyrano[4,3-b]chromenes

A mixture containing aldehyde (1 mmol), *β*-naphthol (1 mmol; 1.44 g), 4-hydroxycoumarin (1 mmol; 1.62 g), 1mmol% of POImD and 10mL H_2O were stirred at room temperature for the required reaction times. The progress of the reaction was monitored by TLC (EtOAc: petroleum ether 1:4). Having completed the reaction, we extracted the product with $CHCl_3$/H_2O. After separation of phases and evaporation of the organic phase and recrystallization of the residue, the pure product was obtained. The aqueous phase was concentrated under reduced pressure to recover the catalyst for subsequent use.

12-(4-Nitrophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4a):

White solid. mp 258–260 °C; FT-IR (KBr): ν 3016, 1729, 1480, 1538, 1250, 1341 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.24 (s, 1H), 7.34-7.51 (m, 5H), 7.61–7.70 (m, 3H), 7.81–7.92 (m, 3H), 8.09 (d, 2H, *J* = 8.6 Hz), 8.19 (d, 1H, *J* = 8.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 36.9, 98.3, 116.2, 116.7, 117.5, 123.3, 123.4, 123.8, 125.8, 125.9, 126.7, 127.3, 128.5, 129.8, 130.2, 130.7, 131.6, 133.5, 146.6, 148.0, 150.7 (C-O), 153.2 (C-O), 160.4 (C-O), 177.3 (C=O) ppm. Anal. calcd for $C_{26}H_{15}NO_5$: C, 74.10; H, 3.59; N, 3.32. Found: C, 74.03; H, 3.65; N, 3.21.

12-(3-Nitrophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one)4b(:

White solid. mp 251-253 °C; FT-IR (KBr): ν 3070, 2931, 1714, 1485, 1573, 1269, 1523, 1350 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.23 (s, 1H), 7.41-7.54 (m, 6H), 7.70 (m, 1H), 7.88 (d, 1H, *J* = 1.2 Hz), 7.92 (d, 2H, *J* = 4.8 Hz), 7.94 (d, 2H, *J* = 8.4 Hz), 8.19 (d, 2H, *J* = 1.6 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 36.2, 99.1, 115.9, 116.7, 117.5, 122.0, 122.9, 123.1, 123.3, 125.5, 125.7, 125.9, 127.8, 128.8, 129.2, 130.4, 130.6, 131.9, 133.7, 134.9, 145.7, 147.5, 148.4 (C-O), 153.0 (C-O), 160.0 (C-O), 176.8 (C=O) ppm. Anal. calcd for $C_{26}H_{15}NO_5$: C, 74.10; H, 3.59; N, 3.32. Found: C, 74.18; H, 3.62; N, 3.27.

12-(4-Cholorophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4c):

White solid. mp 267-269 °C; FT-IR (KBr): ν 3072, 1708, 1637, 1488, 1506, 1577, 1267, 1226, 1093, 813 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.10 (s, 1H), 7.20 (dd, 2H, *J* = 8.8 Hz, *J* = 2.8 Hz), 7.42-7.50 (m, 6H), 7.67 (t, 1H, *J* = 8.4 Hz), 7.86-7.98 (m, 3H), 8.10 (d, 1H, *J* = 8.4 Hz), 8.20 (dd, 1H, *J* = 8.0 Hz, *J* = 6.4 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.9, 99.8, 117.0, 117.4, 122.7, 123.3, 123.4, 124.3, 125.4, 125.6, 126.0, 127.5, 128.6, 129.8, 130.0, 130.9, 131.8, 132.5, 133.5, 142.2 (C-Cl), 147.4 (C-O), 153.0 (C-O), 160.0 (C-O), 176.9 (C=O) ppm. Anal. calcd for $C_{26}H_{15}ClO_3$: C, 76.01; H, 3.68. Found: C, 76.05; H, 3.71.

12-(2-Cholorophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4d):

White solid. mp 238-240 °C; FT-IR (KBr): ν 3056, 2929, 1714, 1643, 1465, 1560, 1612, 1224, 1035, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40 (s, 1H), 7.05-7.12 (m, 2H), 7.35-7.57 (m, 7H), 7.67 (t, 1H, *J* = 9.2 Hz), 7.82-7.88 (m, 12H), 8.20 (dd, 1H, *J* = 8.0 Hz, *J* = 1.2 Hz), 8.27 (d, 1H, *J* = 8.4 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 34.6, 99.5, 116.5, 117.3, 123.2, 123.8, 124.1, 125.3, 125.4, 126.0, 127.1, 127.5, 128.1, 128.6, 129.8, 130.1, 131.3, 131.6, 133.4, 141.1 (C-Cl), 147.2 (C-O), 152.9 (C-O), 160.3 (C-O), 176.7 (C=O) ppm. Anal. calcd for $C_{26}H_{15}ClO_3$: C, 76.01; H, 3.68. Found: C, 75.93; H, 3.61.

e-mail: Nikpassand@iaurasht.ac.ir

12-(4-Bromophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4f):

White solid. mp 287-289 °C; FT-IR (KBr): ν 3072, 1708, 1635, 1463, 1546, 1226, 1267 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.02 (s, 1H), 7.41 (s, 4H), 7.47-7.57 (m, 3H), 7.64 (d, 1H, *J* = 8.8 Hz), 7.71-7.74 (m, 1H), 7.80-7.86 (m, 1H), 8.0-8.09 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.8, 105.2, 113.4, 116.1, 116.9, 117.0, 117.1, 118.3, 120.9, 123.8, 125.2, 125.5, 128.0, 129.2, 130.9, 131.0, 131.6, 131.9, 133.8, 141.3 (C-Br), 152.5 (C-O), 153.9 (C-O), 160.1 (C-O), 176.0 (C=O) ppm. Anal. calcd for $C_{26}H_{15}BrO_3$: C, 68.59; H, 3.32. Found: C, 68.65; H, 3.26.

12-(4-Fluorophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4g)|:

White solid. mp 241-243 °C; FT-IR (KBr): ν 3132, 1700, 1600, 1650, 1481, 1508, 1564, 1240, 1255 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.11 (s, 1H), 6.88-6.92 (m, 2H), 7.41-7.50 (m, 7H), 7.64-7.69 (m, 1H), 7.85-7.90 (m, 2H), 7.97 (d, 1H, *J* = 8.0 Hz), 8.22 (dd, 1H, *J* = 8.0 Hz, *J* = 1.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.5, 115.1, 115.3, 116.5, 117.3, 122.7, 123.9, 125.3, 125.5, 125.9, 127.5, 128.6, 129.7, 129.9, 130.0, 130.9, 131.8, 141.4 (C-O), 145.5 (C-O), 148.3 (C-F), 152.9 (C-O), 176.9 (C=O) ppm. Anal. calcd for $C_{26}H_{15}FO_3$: C, 79.18; H, 3.83. Found: C, 79.13; H, 3.79.

12-Phenyldibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4i):

White solid. mp 276-278 °C; FT-IR (KBr): ν 3056, 3022, 2920, 1718, 1641, 1463, 1575, 1610, 1222, 1271, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.0 (s, 1H), 7.10 (t, 1H, *J* = 7.2 Hz), 7.22 (t, 2H, *J* = 7.6 Hz), 7.49 (dd, 2H, *J* =7.2 Hz), 7.52-7.57 (m, 4H), 7.62 (d, 1H, *J* = 9.2 Hz), 7.72 (d, 1H , *J* = 9.2 Hz), 7.82 (t, 1H, *J* = 6.8 Hz), 7.99-8.12 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 36.7, 106.0, 113.6, 116.7, 117.0, 117.3, 117.4, 118.2, 119.0, 120.2, 122.3, 124.2, 124.5, 127.5, 129.5, 130.0, 130.1, 131.2, 133.7, 138.8, 152.7 (C-O), 153.4 (C-O), 160.2 (C-O), 173.2 (C=O) ppm. Anal. calcd for $C_{26}H_{16}O_3$: C, 82.96; H, 4.28. Found: C, 83.02; H, 4.21.

12-(4-Methylphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4j):

White solid. mp 225-227 °C; FT-IR (KBr): ν 3018, 2920, 1714, 1639, 1463, 1510, 1566, 1224 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3H), 5.73 (s, 1H) 7.0-7.04 (m, 2H), 7.27-7.30 (m, 2H), 7.46-7.55 (m, 4H), 7.74 (d, 2H, *J* = 9.2 Hz), 8.01-8.08 (m, 3H), 8.17 (dd, 1H, *J* =7.6 Hz, *J* = 0.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.2, 34.6, 105.9, 114.2, 116.0, 117.1, 117.3, 117.4, 118.0, 120.0, 122.1, 124.3, 125.0, 127.2, 128.8, 130.0, 130.5, 131.4, 132.0, 135.0, 140.2, 153.3 (C-O), 154.4 (C-O), 161.4 (C-O), 174.7 (C=O) ppm. Anal. calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 83.12; H, 4.61.

12-(2,3-Dimethylphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4k):

White solid. mp 257-258 °C; FT-IR (KBr): ν 3018, 1682, 1636, 1543, 1452, 1319, 1242 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.78 (s, 3H), 2.32 (s, 3H), 6.63 (s, 1H), 7.06–7.08 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.32–7.37 (m, 2H), 7.42 (d, 1H, *J* = 8.2 Hz), 7.51 (t, 1H, *J* = 8.2 Hz), 7.65 (t, 1H, *J* = 8.4 Hz), 7.79 (d, 1H, *J* = 8.4 Hz), 7.89 (d, 1H, *J* = 8.4 Hz), 7.92 (d, 1H, *J* = 8.2 Hz), 8.11 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.2, 20.6, 36.5, 98.8, 105.7, 112.9, 116.1, 116.3, 118.7, 119.6, 122.9, 122.3, 123.6, 124.2, 125.6, 126.0, 127.6, 128.1, 129.5, 132.6, 133.2, 134.2, 136.6, 147.5 (C-O), 151.3 (C-O), 162.6 (C-O), 176.9 (C=O) ppm. Anal. calcd for $C_{28}H_{20}O_3$: C, 83.15; H, 4.98. Found: C, 83.03; H, 5.06.

12-(4-Methoxyphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4l):

White solid. mp 211-213 °C; FT-IR (KBr): ν 3064, 2941, 1712, 1641, 1461, 1508, 564, 1174, 1240, 811 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.35 (s, 3H), 5.92 (s, 1H), 6.77 (t, *J* = 8.8 Hz, 2H), 7.29-7.32 (m, 2H), 7.48-7.55 (m, 3H), 7.60 (d, 1H, *J* = 9.2 Hz), 7.68-7.72 (m, 2H), 7.96-8.09 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.8, 62.2, 105.8, 113.8, 115.5, 116.5, 117.8, 118.1, 118.7, 121.4, 123.0, 124.4, 125.0, 127.5, 128.5, 129.9, 130.7, 132.6, 133.9, 138.1, 146.3 (C-O), 154.5 (C-O), 155.6 (C-O), 160.3 (C-O), 175.5 (C=O) ppm. Anal. calcd for $C_{27}H_{18}O_4$: C, 79.79; H, 4.46. Found: C, 79.85; H, 4.41.

12-(3, 4, 5-Trimethoxyphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4n):

White solid. mp 201-203 °C; FT-IR (KBr): ν 3054, 1704, 1639, 1538, 1472, 1352, 1242 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (s, 3H), 3.61 (s, 6H), 5.75 (s, 1H), 6.69 (d, 2H, *J* = 8.6 Hz), 7.42–7.58 (m, 4H), 7.70–7.76 (m, 2H), 8.02 (d, 1H, *J* = 8.2 Hz), 8.11 (d, 1H, *J* = 8.6 Hz), 8.24 (t, 2H, *J* = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.4, 56.25, 56.8, 56.3, 98.9, 115.3, 116.5, 117.5, 121.2, 122.5, 123.4, 125.6, 127.2, 128.9, 129.0, 130.2, 131.4, 134.5, 135.1, 145.3 (C-O), 146.7 (C-O), 147.1 (C-O), 152.9 (C-O), 159.2 (C-O), 175.4 (C=O) ppm. Anal. calcd for $C_{29}H_{22}O_6$: C, 74.67; H, 4.75. Found: C, 74.78; H, 4.83.

12-(4-Dimethylaminophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4o):

White solid. mp 255-257 °C; FT-IR (KBr): ν 3074, 2914, 1656, 1521, 1560, 1660, 1346, 1191, 810 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 6H), 5.60 (s, 1H), 7.22-7.39 (m, 8H), 7.50-7.52 (m, 1H), 7.63-7.68 (m, 1H), 7.80-7.84 (m, 3H), 8.01 (d, 1H, *J* = 8.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.0, 52.4, 105.7, 113.0, 115.2, 116.1, 117.2, 117.9, 118.2, 121.9, 123.4, 125.0, 126.8, 128.6, 129.0, 132.1, 133.0, 133.6, 136.2, 137.0, 142.3 (C-N), 154.2 (C-O), 155.0 (C-O), 158.5 (C-O), 173.4 (C=O) ppm. Anal. calcd for $C_{28}H_{21}NO_3$: C, 80.17; H, 5.05; N, 3.34. Found: C, 80.24; H, 4.99; N, 3.29.

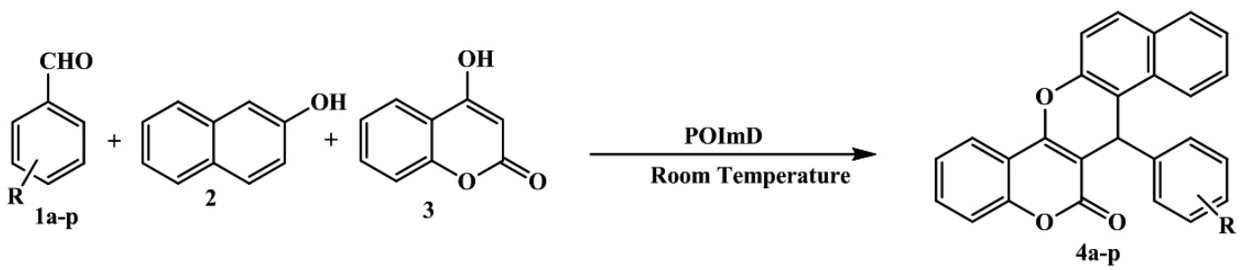
12-(4-Hydroxyphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4p):

White solid. mp 298-300 °C; FT-IR (KBr): ν 3281, 3012, 1706, 1635, 1551, 1462, 1301, 1203 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72 (s, 1H), 7.60 (d, 1H, *J* = 8.6 Hz), 7.63–7.70 (m, 3H), 7.87 (t, *J* = 8.6 Hz, 1H), 7.90 (d, 3H, *J* = 8.4 Hz), 8.05 (d, 3H, *J* = 8.2 Hz), 8.13 (t. 2H, *J* = 8.2 Hz), 8.21 (d, 1H, *J* = 8.2 Hz), 9.31 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.8, 98.4, 112.5, 116.2, 118.4, 122.5, 123.3, 123.7, 126.2, 127.8, 128.5, 128.9, 130.4, 130.8, 131.3, 131.9, 135.0, 140.3, 140.4, 149.6, 152.0 (C-O), 152.5 (C-O), 156.0 (C-O), 162.3 (C-O), 175.2 (C=O) ppm. Anal. calcd for $C_{26}H_{16}O_4$: C, 79.58; H, 4.11;. Found: C, 79.66; H, 4.03.

RESULTS AND DISCUSSION

In continuation of our ongoing studies to synthesize heterocyclic and pharmaceutical compounds by mild and practical protocols [25-28], herein we wish to report our experimental results on the synthesis of pyrano[4,3-*b*]chromenes, using various aromatic aldehydes, 2-naphthol and 4-hydroxycoumarin in the presence of POImD in aqueous media at room temperature (Scheme 1).

The reaction between 4-nitrobenzaldehyde, 2-naphthol and 4-hydroxycoumarin in the presence of different catalysts was carried out as a model. All the reactions were carried out with catalytic amounts of catalysts. As described in Table 1, the higher yield, shorter reaction time and milder reaction condition gained with 0.01mmol of POImD (Table 1; Entry 13).



Scheme 1. Synthesis of pyrano[4,3-*b*]chromenes using POImD

As shown in Table 1 the ability and efficiency of ionic liquids such as [BMIM]Br, [BMIM]OH and [DBU]OAc and organometallic catalyst potassium phthalimide (PPI) [29] are somewhat similar, while organometallic catalyst potassium 2-oxoimidazolidine-1,3-diide (POImD) is more efficient for the synthesis of pyrano[4,3-*b*]chromenes. The catalysts POImD, rather than others, can decrease the reaction time more. It is because of the presence of four ionic centers in POImD, in comparison with two ionic centers in [BMIM]Br, [BMIM]OH, [DBU]OAc and PPI which helps ionic catalyst POImD have more abilities so as to be applied for the polarization of aldehydes.

On the other hand, as shown in Table 1, the previously reported synthesis of pyranochromene was carried out in high temperature [29-32], but in this current method we synthesize these collections of compounds at room temperature in mild conditions.

Apart from the mild conditions of the process and its excellent results, the simplicity of product isolation and the possibility to recycle the catalyst offer a significant advantage. A Comparison of efficiency of this method with some of previous reported methods for the synthesis of **4a** was carried out (Table 1; Entries 9-12).

Table 1. Effect of catalyst on the synthesis of **4a.**

Entry	Catalyst	Catalyst loading (mmol%)	Reaction condition[a]	Time (min)	Yield (%)[b]
1	HCl	4drops	reflux	840	52
2	SiO_2	2	reflux	360	65
3	K10	0.2g	reflux	240	71
4	nano-Fe_3O_4	2	reflux	720	48
5	$ZnCl_2$	2	reflux	360	63
6	[BMIM]Br	2	neat, r.t.	180	80
7	[BMIM]OH	2	neat, r.t.	170	79
8	[DBU]OAc	2	neat, r.t.	175	82
9	$Zr(HSO_4)_4$ [30]	5	110°C	25	89
10	MTSA [32]	2	120°C	60	88
11	$[Bpy]BF_4$ [31]	4	80°C	120	85
12	PPI [29]	15	reflux	30	95
13	POImD	10	r.t.	30	97
14	POImD	5	r.t.	30	96
15	POImD	1	r.t.	30	97

[a.] solvent in the entries 1-5, 9 and 11-15 was 10mL of distillated water. [b.] Isolated yield after recrystallization

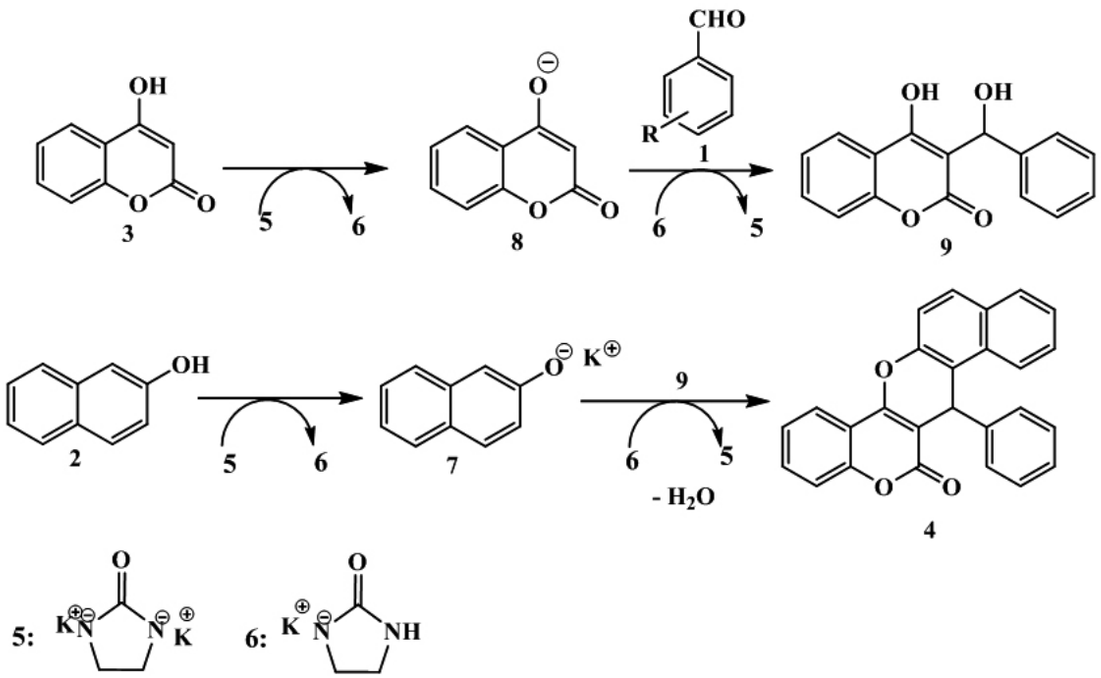
To investigate the efficiency and generality of the reaction, various benzaldehydes were combined with 2-naphthol and 4-hydroxycoumarin in the presence of POImD in aqueous media at room temperature. The results are summarized in Table 2.

Table 2. Synthesis of pyrano[4,3-*b*]chromenes **4a-p** using POImD

Entry	Product	R	Time (min)	Yield (%)[a]	Found Mp (°C)	Reported Mp (°C)
1	**4a**	4-NO_2	30	97	258–260	257–258[32]
2	**4b**	3-NO_2	40	91	231–233	237–23833
3	**4c**	4-Cl	45	89	267–269	267–268[32]
4	**4d**	2-Cl	60	88	238–240	240–241[33]
5	**4e**	2,4-Cl_2	45	92	267–269	267–268[32]
6	**4f**	4-Br	75	92	287–289	281–282[33]
7	**4g**	4-F	30	90	241–243	245–246[33]
8	**4h**	4-F	30	93	276–278	282–283[33]
9	**4i**	H	60	87	276–278	280–282[32]
10	**4j**	4-CH_3	60	86	225–227	230–231[32]
11	**4k**	2,3-$(CH_3)_2$	120	84	257–258	267–268[33]
12	**4l**	4-OCH_3	120	83	211–213	214–215[32]
13	**4m**	2-OCH_3	90	82	214–216	211–212[33]
14	**4n**	3,4,5-$(OCH_3)_3$	90	86	201–203	196–197[33]
15	**4o**	4-$N(CH_3)_2$	120	85	255–257	257–258[32]
16	**4p**	4-OH	120	86	298–300	299–300[33]

[a.] Isolated yield

We propose a possible mechanism for synthesis of pyrano[4,3-*b*] chromene derivatives (Scheme 2). In a plausible mechanism, potassium 2-oxoimidazolidine-1,3-diide (POImD) (**5**) converted 4-hydroxycoumarin (**3**) to active form **8** by hydrogen abstraction. Then, the nucleophilic attack of C-3 anion **8** via resonance, electron density at the C-1 position transferred to the C-3 of intermediate **7** to arylaldehyde (**1**) lead to compound **9**. Finally, after nucleophilic addition of 2-naphtholate **7** following by dehydration, compound **9** was conformed to product **4**. It is mentionable that under this procedure catalyst POImD reversibly converts from **5** to **6**.



Scheme 2. Possible mechanism for synthesis of pyrano[4,3-*b*]chromenes

After completion of reaction, the catalyst is easily separated from the reaction medium by evaporation of aqueous media. The washed catalyst is dried under vacuum to recover for reuse in subsequent reactions. After five successive runs, recycled POImD showed no loss of efficiency with regard to reaction time and yield (Table 3).

Table 3. Evaluation of reusability of catalyst for the synthesis of **4a**

run	1	2	3	4	5
Time(min)	30	30	30	30	30
Yield(%)	97	96	95	97	95

CONCLUSIONS

Finally, we developed an efficient, novel, green, fast and convenient procedure for the three component synthesis of pyrano[4,3-*b*]chromenes through cyclocondensation reaction of *β*-naphthol, aldehydes and 4-hydroxycoumarin, using POImD as a novel and reusable organometallic catalyst. The remarkable advantages offered by this method are that catalyst is inexpensive, non-toxic, easy to handle and reusable. Simple work-up procedure, short reaction time, high yields of product with better purity and green aspect by avoiding toxic catalyst and hazardous solvent. To the best of our knowledge, this is the first report on synthesis of pyrano[4,3-*b*]chromenes derivatives using potassium 2-oxoimidazolidine-1,3-diide (POImD).

ACKNOWLEDGEMENTS

Financial support by Rasht Branch, Islamic Azad University is gratefully acknowledged.

REFERENCES

1. (a). H. Miao, Z. Yang, Org. Lett. 2, 1765, (2000); (b). A. Akbari, A. Hosseini-Nia, Iranian J. Org. Chem. 6, 1183, (2014).
2. (a). P. Kumar, M. S. Bodas, Org. Lett. 2, 3821, (2000); (b). N. Thomas, S. M. Zachariah Asian J. Pharm. Clinic. Res. 6, 11, (2013).
3. T. A. Bayer, S. Schafer, H. Breyh, O. Breyhan, C. Wirths, G. A. Treiber, Multhaup, Clin Neuropathol. 25, 163, (2006).
4. (a). B. M. Trost, Chem. Int. Ed. Engl. 34, 259, (1995); (b). M. El-Agrody, A. M. Fouda, E. S. A. E. H. Khattab, Med. Chem. Res. 22, 6105, (2013).
5. Sh. Jain, P. K. Paliwal, G. N. Babu, A. Bhatewara, J. Saudi Chem. Soc. 18, 535, (2014).
6. A. M. M. El-Saghier, M. B. Naili, B. K. Rammash, N. A. Saleh, K. M. Kreddan, Arkivoc xvi 83, (2014).
7. W. O. Foye, Principidi Chimica Farmaceutica Piccin- Padova, 1991, Italy.
8. E. A. A. Hafez, M. H. Elnaghi, A. G. A. Elagamey, F. M. A. A. El-Taweel, Heterocycles. 26, 903, (2004).
9. A. Bolognese, G. Correale, M. Manfra, A. Levecchia, O. Mazzoni, E. Novellino, P. Lacolla, G. Sanna, R. Loddo, J. Med. Chem. 47, 849, (2004).
10. (a). G. P. Ellis, The Chemistry of Heterocyclic Compounds. In Chromenes; Chromenes, and Chromenes; Weissberger; Taylor, A.; Eds, E. C.; John Wiley; NewYork. Chapter 2, 11, (1977); (b). M. Kidwai, S. Saxen, M. K. R. Khan, S. S. Thukral, Bioorg. Med. Chem. Lett. 15, 4295, (2005).
11. T. Hanamoto, K. Shindo, M. Matsuoka, Y. Kiguchi, M. Kondo, J. Chem. Soc., Perkin Trans. 1, 3082, (2000).
12. P. T. Kaye, X. W. Nocanda, J. Chem. Soc., Perkin Trans. 1, 1331, (2000).
13. H. H. Jardosh, M. P. Patel, Med. Chem. Res. 22, 905, (2012).
14. K. A. Parker, T. L. Mindt, Org. Lett. 3, 3875, (2001).

15. B. V. S. Reddy, S. Jalal, P. Borkar, J. S. Yadav, P. P. Reddy, A. C. Kunwar, B. Sridhar, Org. Biomol. Chem. 10, 656, (2012).
16. S. Chang, R. H. Grubbs, J. Org. Chem. 63, 864, (1998).
17. (a) Q. Wang, M. G. Finn, Org. Lett. 2, 4063, (2000); (b) G. W. Kabalka, B. Venkataiah, B. C. Das, Synlett. 2194, (2004).
18. M. Iyer, G. R. Trivedi, Synth. Commun. 20, 1347, (1990).
19. R. S. Varma, R. Dahiya, J. Org. Chem. 63, 8038, (1998).
20. J. Hlubucek, E. Ritchie, W. C. Taylor, Tetrahedron Lett. 10, 1369, (1969).
21. L. W. Ye, X. L. Sun, C. Y. Zhu, Y. Tang, Org. Lett. 8, 3853, (2006).
22. U. M. Lindstrom, Chem. Reviews, 102, 2751, (2002).
23. Z. B. Xu, J. Qu, Chem. A Euro. J. 19, 314, (2013).
24. S. Chitra, N. Paul, S. Muthusubramanian, P. Manisankar, Green Chem. 13, 2777, (2011).
25. ***M.*** Nikpassand, L. Zare Fekri, M. R. Mousavi, Lett. Org. Chem. 9, 375, (2012).
26. M. Nikpassand, M. Mamaghani, F. Shirini, K. Tabatabaeian, Ultrason. sonochem. 17, 301, (2010).
27. ***M.*** Nikpassand, L. Zare Fekri, M. Gharib, O. Marvi, Lett. Org. Chem. 9, 745, (2012).
28. M. Nikpassand, D. Pirdelzendeh, Dyes Pig. 130, 314, (2016).
29. H. Kiyani, F. Ghorbani, Jordan J. Chem. 9, 1, (2014).
30. X. Wang, G. Lu, F. Yan, W. Ma, L. Wu, J. Hetero. Chem. 48, 1379, (2011).
31. Y. Wan, C. Wang, H. Wang, L. Zhao, X. X. Zhang, J. J. Shi, S. Huang, G. X. Liu, H. Wu, J. Heterocyclic Chem. 51, 1293, (2014).
32. W. Ma, X. Wang, F. Yan, L. Wu, Y. Wang, Monatshefte fur Chemie, 142, 163, (2011).