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Synthesis of a novel series of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-ones, indeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one, and indeno [1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione catalyzed by reusable polyvinylpolypyrrolidone-supported triflic acid

Syed Sheik Mansoor · Majid Ghashang

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Abstract Polyvinylpolypyrrolidone-supported triflic acid (PVPP.OTf) has been used as a recyclable catalyst for synthesis of a series of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one derivatives by condensation of aldehydes, resorcinol, and 2*H*-indene-1,3-dione. 13-Phenylindeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one and 12-phenyl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione were also synthesized by condensation of benzaldehyde, *β*-naphthol or 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione with PVPP.OTf as catalyst. The heterogeneous catalyst was used for four runs. This method has the advantages of high yields, simple methodology, short reaction times, and easy work-up.

Keywords Polyvinylpolypyrrolidone-supported triflic acid (PVPP.OTf) · Indeno[1,2-*b*]chromen-11-one · 2*H*-Indene-1,3-dione · Recyclable catalyst

Introduction

Multi-component reactions (MCRs) have become very popular for discovery of biologically active novel compounds and are of great interest in diversity-oriented synthesis, especially generation of compound libraries for screening purposes [1]. The development of environmentally benign, efficient, and economical methods for synthesis of biologically interesting compounds remains a significant challenge in synthetic chemistry. Performing MCRs in water as reaction medium is one of the

S. S. Mansoor (✉)
Bioactive Organic Molecule Synthetic Unit, Research Department of Chemistry, C. Abdul Hakeem College, Melvisharam 632 509, Tamil Nadu, India
e-mail: smansoors2000@yahoo.co.in

M. Ghashang
Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Esfahan, Iran

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most suitable methods, and a major aspect of green chemistry, because they enable simple and rapid access to a large number of organic molecules by sustainable methods [2, 3].

In recent years, 4*H*-pyrans and their derivatives have attracted much interest because of their useful biological and pharmacological activity, for example anticoagulant, spasmolytic, anticancer, and antianaphylactin properties [4]. Furthermore, substituted 4*H*-pyrans also constitute structural units of several natural products [5]. The 4*H*-pyrans also antitumor [6], antibacterial [7], antioxidant [8], antigenotoxic [9], and antiangiogenic activity [10].

Considering the importance of these compounds, numerous methods have been reported for synthesis of 4*H*-pyran derivatives with a variety of catalysts, for example CuO–CeO_2 nanocomposite [11], carbon-based solid acid [12], tetramethylammonium hydroxide [13], SB-DABCO [14], silica-bonded *N*-propylpiperazine sodium *n*-propionate [15], silica nanoparticles [16], and DBU under microwave-irradiation [17].

Among different pyran structures, the indenopyran nucleus, in particular, is a "privileged medicinal scaffold" used for development of pharmaceutical agents with a variety of applications [7, 18–20]. Compounds containing this structure have a wide range of pharmacological properties, including antidepressant [21], antiulcer [22], and antiallergenic [23] activity. Consequently, methods for synthesis of novel indenopyrans are of particular interest to organic and medicinal chemists [24–26].

Trifluoromethanesulfonic acid or triflic acid is a well known Brønsted superacid which has been extensively studied as a catalyst in a wide range of organic transformations, including stereoselective Friedel–Crafts aminoalkylation of indoles and pyrroles [27], annelation of aromatic sulfonamides [28], synthesis of *β*-acetamido ketones [29], acylation of alcohols [30], cyclization of unsaturated alcohols [31], and addition of allylboranes to aldehydes [32].

However, TfOH is highly corrosive and is a fuming liquid, so there are difficulties involved in storage, transportation, handling, and waste disposal, thus severely restricting its application in industry. Immobilization of triflic acid on inorganic materials, for example silica gel, affords solid acids that can be easily handled, because they are invariably low-toxicity, non-corrosive, free-flowing powders with superior thermal and mechanical stability under catalytic conditions. Silica gel-supported triflic acid is readily prepared by simple absorption of TfOH on chromatographic silica gel. This solid acid has been used as an efficient catalyst for heterogeneous addition of a variety of *β*-dicarbonyl compounds to alcohols and alkenes, affording moderate to excellent yields under solvent-free conditions or in nitromethane. Moreover, this silica gel supported catalyst results in higher reaction yields than homogeneous catalysts and can be readily recovered and reused up to six times with almost unchanged reactivity and yields [33]. Processes for immobilization of TfOH on solid supports have already been reported [34–37].

Polymer-supported reagents have attracted much attention in recent years for development of novel organic reaction methods [38, 39], because their heterogeneous nature enables reactions to be conducted under mild conditions and the organic products to be isolated with relative ease from the reaction media.

Furthermore, the toxicity of these systems is low. Taken together, the special properties associated with polymeric reagents prompted us to investigate their application to organic synthesis.

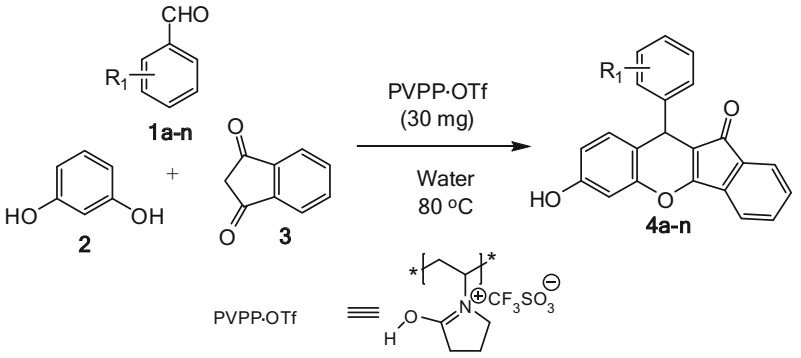
Polyvinylpolypyrrolidone has strong binding affinity for small molecules. An efficient procedure for acetylation of alcohols and phenols with acetic anhydride in the presence of a catalytic amount of polyvinylpolypyrrolidone tribromide has been successfully developed [40]. Trimethylsilylation of alcohols has been achieved with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as silylating agent, in the presence of polyvinylpolypyrrolidone tribromide in acetonitrile at room temperature [41]. Polyvinylpolypyrrolidone-supported boron trifluoride (PVPP-BF_3) has been studied for synthesis of 4-methylcoumarin by the Pechmann reaction [42], for synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes and bis(naphthalen-2-yl-sulfane) derivatives [43], for preparation of amides by reaction of nitriles with benzhydrol and tertiary alcohols [44], and for oxidation of sulfides to sulfones in the presence of 35 % hydrogen peroxide [45]. Polyvinylpolypyrrolidone-supported hydrogen peroxide (PVP-H_2O_2), silica–sulfuric acid (SiO_2OSO_3H), and catalytic amounts of ammonium bromide (NH_4Br) have been introduced as green media for in-situ generation of the bromonium ion (Br^+), which was used for selective oxidation of sulfides and alcohols to sulfoxides and carbonyl compounds, respectively [46]. Polyvinylpolypyrrolidone-supported triflic acid (PVPP.OTf) has recently attracted much attention as an efficient catalyst for construction of carbon–carbon and carbon–heteroatom bonds [47–49], because of its eco-friendly nature, ease of handling, high reactivity, and easy work-up procedures. PVPP.OTf has been reported as a recyclable heterogeneous solid-acid catalyst for synthesis of tetrahydrobenzo[*a*]xanthen derivatives [47], synthesis of *bis*-indolyl methane derivatives [48], and synthesis of quinoxaline derivatives [49].

As a continuation of our studies on the use of solid catalysts in organic transformations [50–53], we report an efficient method for synthesis of a series of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one derivatives, with polyvinylpolypyrrolidone-supported triflic acid (PVPP.OTf) as catalyst, by three-component condensation of aromatic aldehydes, resorcinol, and 2*H*-indene-1,3-dione in water at 80 °C (Scheme 1). We have also used PVPP.OTf as catalyst for condensation of benzaldehyde, *β*-naphthol or 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione for synthesis of 13-phenylindeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one and 12-phenyl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione under similar conditions (Scheme 2).

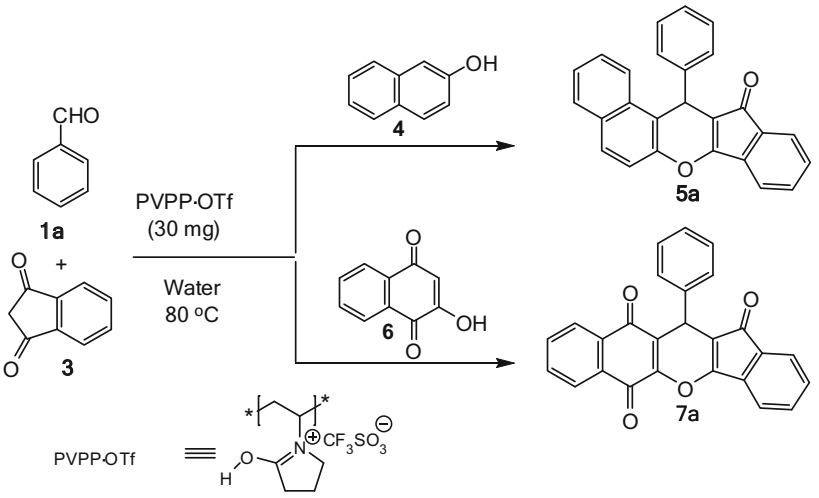
Experimental

Apparatus and analysis

Chemicals were purchased from Merck, Fluka, and Aldrich. All yields refer to isolated products unless otherwise stated. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained by use of a Bruker DRX-500 Avance at ambient temperature, with TMS as internal standard. FT-IR spectra were obtained as KBr discs by use of a Shimadzu spectrometer. Mass spectra were acquired by use of a



Scheme 1 Reaction of aldehyde, resorcinol, and 2*H*-indene-1,3-dione for synthesis of a series of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one derivatives



Scheme 2 Reaction of benzaldehyde, *β*-naphthol or 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione for synthesis of 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one and 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione

Varian Saturn 2000 GC–MS instrument. Elemental analysis were performed by means of a Perkin–Elmer 2400 CHN elemental analyzer.

Preparation of polyvinylpolypyrrolidone triflate (PVPP.OTf)

Polyvinylpolypyrrolidone triflate was prepared as reported elsewhere [47]. TfOH (2.0 g, 13 mmol) was added to a suspension of polyvinylpolypyrrolidone (3.0 g) in toluene (35 mL) and the mixture was stirred magnetically for 60 min at room temperature. The toluene was removed under reduced pressure and the residue was dried at 110 °C for 2 h to afford PVPP.OTf as a white powder. The number of H^+ sites on PVPP.OTf, determined by acid–base titration, was 10 mequiv/g.

General procedure for preparation of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one derivatives

A mixture of aldehyde (1 mmol), resorcinol (1 mmol), and 2*H*-indene-1,3-dione (1 mmol) was added to PVPP.OTf (30 mg), and the mixture was stirred at 80 °C in 5 ml water for an appropriate time. The reaction was monitored by TLC. On completion of the reaction the mixture was diluted with CH_2Cl_2 (20 mL), and filtered to recover the catalyst. The filtrate was then collected and evaporated to dryness to give the crude product, which was purified by silica gel column chromatography with CH_2Cl_2 as mobile phase.

Spectral data for compounds **4a–n**

*7-Hydroxy-10-phenyl-10H-indeno[1,2-b]chromen-11-one (**4a**)*

IR (KBr, cm^{-1}): 3,444, 2,977, 1,655, 1,596, 1,377, 1,222, 1,198, 1,074, 795; ^1H NMR (500 MHz, DMSO-d_6): δ 4.66 (s, 1H, CH), 6.62 (d, $J = 4.2$ Hz, 1H, Ar–H), 6.80 (dd, $J = 4.2$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.92 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.14–7.30 (m, 5H, Ar–H), 7.70–7.88 (m, 4H, Ar–H), 9.69 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.2, 104.5, 105.1, 110.7, 124.3, 125.9, 126.6, 128.3, 128.7, 129.7, 130.2, 134.3, 135.0, 136.6, 144.0, 156.0, 159.0, 162.7, 189.3 ppm. MS (ESI): *m/z* 327 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.98; H, 4.29 %. Found: C, 80.87; H, 4.24 %.

*7-Hydroxy-10-(4-chlorophenyl)-10H-indeno[1,2-b]chromen-11-one (**4b**)*

IR (KBr, cm^{-1}): 3,438, 2,972, 1,652, 1,597, 1,378, 1,224, 1,194, 1,066, 812; ^1H NMR (500 MHz, DMSO-d_6): δ 4.65 (s, 1H, CH), 6.61 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.81 (dd, $J = 4.1$ Hz, $J = 8.0$ Hz, 1H, Ar–H), 6.94 (d, $J = 8.0$ Hz, 1H, Ar–H), 7.11 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.34 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.73–7.89 (m, 4H, Ar–H), 9.74 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.1, 104.1, 104.8, 111.0, 124.5, 125.8, 126.5, 128.5, 128.9, 129.5, 130.7, 134.4, 135.1, 136.3, 144.1, 156.2, 159.2, 162.5, 189.0 ppm. MS (ESI): *m/z* 361.4 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}ClO_3$: C, 73.24; H, 3.61 %. Found: C, 73.19; H, 3.57 %.

*7-Hydroxy-10-(4-methylphenyl)-10H-indeno[1,2-b]chromen-11-one (**4c**)*

IR (KBr, cm^{-1}): 3,442, 2,966, 1,647, 1,590, 1,375, 1,227, 1,193, 1,065, 816; ^1H NMR (500 MHz, DMSO-d_6): δ 2.14 (s, 3H, CH_3), 4.59 (s, 1H, CH), 6.64 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.83 (dd, $J = 4.1$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.93 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.09 (d, 2H, $J = 8.1$ Hz, Ar–H), 7.30 (d, 2H, $J = 8.1$ Hz, Ar–H), 7.69–7.85 (m, 4H, Ar–H), 9.76 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.9, 31.2, 104.0, 104.6, 111.1, 124.2, 126.2, 126.8, 128.2, 128.9, 129.3, 130.4, 134.4, 134.9, 136.1, 144.0, 155.7, 158.6, 162.3, 188.7 ppm. MS (ESI): *m/z* 341 $[M + H]^+$. Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.18; H, 4.71 %. Found: C, 81.11; H, 4.67 %.

*7-Hydroxy-10-(4-methoxyphenyl)-10H-indeno[1,2-b]chromen-11-one (**4d**)*

IR (KBr, cm^{-1}): 3,430, 2,968, 1,648, 1,590, 1,375, 1,219, 1,192, 1,070, 788; ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.64 (s, 3H, OCH_3), 4.60 (s, 1H, CH), 6.68 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.80 (dd, $J = 4.1$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.92 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.21 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.32 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.71–7.83 (m, 4H, Ar–H), 9.66 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 30.9, 54.9, 104.3, 105.1, 110.7, 124.1, 126.3, 126.8, 128.4, 128.8, 129.2, 130.5, 134.3, 134.9, 136.2, 143.7, 155.4, 158.7, 162.4, 188.5 ppm. MS (ESI): *m*/*z* 357 $[M + H]^+$. Anal. Calcd. for $C_{23}H_{16}O_4$: C, 77.53; H, 4.49 %. Found: C, 77.50; H, 4.45 %.

*7-Hydroxy-10-(4-bromophenyl)-10H-indeno[1,2-b]chromen-11-one (**4e**)*

IR (KBr, cm^{-1}): 3,436, 2,969, 1,640, 1,591, 1,374, 1,218, 1,189, 1,077, 794; ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.66 (s, 1H, CH), 6.67 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.82 (dd, $J = 4.1$ Hz, $J = 8.1$ Hz, 1H, Ar–H), 6.91 (d, $J = 8.1$ Hz, 1H, Ar–H), 7.18 (d, 2H, $J = 8.1$ Hz, Ar–H), 7.39 (d, 2H, $J = 8.1$ Hz, Ar–H), 7.75–7.88 (m, 4H, Ar–H), 9.78 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 30.8, 103.9, 104.8, 110.5, 124.4, 126.4, 126.9, 128.6, 128.9, 129.6, 130.6, 134.6, 135.2, 136.4, 143.5, 155.6, 158.7, 162.2, 188.3 ppm. MS (ESI): *m*/*z* 405.8 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}BrO_3$: C, 65.20; H, 3.21 %. Found: C, 65.12; H, 3.19 %.

*7-Hydroxy-10-(4-nitrophenyl)-10H-indeno[1,2-b]chromen-11-one (**4f**)*

IR (KBr, cm^{-1}): 3,438, 2,973, 1,651, 1,595, 1,373, 1,219, 1,189, 1,075, 822; ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.62 (s, 1H, CH), 6.63 (d, $J = 4.2$ Hz, 1H, Ar–H), 6.81 (dd, $J = 4.2$ Hz, $J = 8.1$ Hz, 1H, Ar–H), 6.90 (d, $J = 8.1$ Hz, 1H, Ar–H), 7.17 (d, 2H, $J = 8.1$ Hz, Ar–H), 7.31 (d, 2H, $J = 8.1$ Hz, Ar–H), 7.74–7.90 (m, 4H, Ar–H), 9.77 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.1, 104.3, 104.9, 110.8, 124.6, 126.1, 126.9, 128.5, 128.8, 129.4, 130.6, 134.7, 135.3, 136.4, 143.6, 155.4, 158.8, 162.7, 188.4 ppm. MS (ESI): *m*/*z* 372 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}NO_5$: C, 71.16; H, 3.50; N, 3.77 %. Found: C, 71.11; H, 3.47; N, 3.78 %.

*7-Hydroxy-10-(4-fluorophenyl)-10H-indeno[1,2-b]chromen-11-one (**4g**)*

IR (KBr, cm^{-1}): 3,433, 2,974, 1,647, 1,594, 1,377, 1,221, 1,187, 1,073, 806; ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.61 (s, 1H, CH), 6.69 (d, $J = 4.2$ Hz, 1H, Ar–H), 6.79 (dd, $J = 4.2$ Hz, $J = 8.0$ Hz, 1H, Ar–H), 6.93 (d, $J = 8.0$ Hz, 1H, Ar–H), 7.19 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.39 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.77–7.94 (m, 4H, Ar–H), 9.69 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.1, 104.2, 104.9, 110.3, 124.8, 126.3, 127.0, 128.3, 128.7, 129.3, 130.4, 134.5, 135.0, 136.5, 143.7, 155.8, 158.9, 162.6, 188.2 ppm. MS (ESI): *m*/*z* 345 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}FO_3$: C, 76.74; H, 3.78 %. Found: C, 76.70; H, 3.75 %.

*7-Hydroxy-10-(3-nitrophenyl)-10H-indeno[1,2-b]chromen-11-one (**4h**)*

IR (KBr, cm^{-1}): 3,443, 2,975, 1,649, 1,590, 1,379, 1,225, 1,190, 1,069, 822; ^1H NMR (500 MHz, DMSO-d_6): δ 4.68 (s, 1H, CH), 6.68 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.81 (dd, $J = 4.1$ Hz, $J = 8.1$ Hz, 1H, Ar–H), 6.92 (d, $J = 8.1$ Hz, 1H, Ar–H), 7.22–7.41 (m, 4H, Ar–H), 7.72–7.84 (m, 4H, Ar–H), 9.73 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.3, 103.9, 104.6, 110.4, 124.4, 126.2, 127.0, 128.3, 128.6, 129.7, 130.2, 134.5, 135.1, 136.7, 143.5, 155.7, 159.0, 162.4, 189.1 ppm. MS (ESI): *m/z* 372 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}NO_5$: C, 71.16; H, 3.50; N, 3.77 %. Found: C, 71.09; H, 3.45; N, 3.74 %.

*7-Hydroxy-10-(2-chlorophenyl)-10H-indeno[1,2-b]chromen-11-one (**4i**)*

IR (KBr, cm^{-1}): 3,441, 2,974, 1,646, 1,593, 1,369, 1,226, 1,189, 1,068, 794; ^1H NMR (500 MHz, DMSO-d_6): δ 4.66 (s, 1H, CH), 6.69 (d, $J = 4.3$ Hz, 1H, Ar–H), 6.82 (dd, $J = 4.1$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.94 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.24–7.40 (m, 4H, Ar–H), 7.78–7.96 (m, 4H, Ar–H), 9.77 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 30.7, 104.2, 104.5, 111.2, 124.3, 125.8, 126.5, 128.3, 128.9, 129.6, 130.9, 134.6, 134.7, 136.3, 143.7, 156.0, 159.2, 162.3, 189.0 ppm. MS (ESI): *m/z* 361.4 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}ClO_3$: C, 73.24; H, 3.61 %. Found: C, 73.16; H, 3.58 %.

*7-Hydroxy-10-(2-fluorophenyl)-10H-indeno[1,2-b]chromen-11-one (**4j**)*

IR (KBr, cm^{-1}): 3,448, 2,972, 1,644, 1,594, 1,366, 1,219, 1,200, 1,070, 830; ^1H NMR (500 MHz, DMSO-d_6): δ 4.60 (s, 1H, CH), 6.64 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.81 (dd, $J = 4.1$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.90 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.20–7.38 (m, 4H, Ar–H), 7.75–7.92 (m, 4H, Ar–H), 9.64 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 30.8, 104.2, 105.2, 110.5, 124.3, 126.0, 126.6, 128.1, 128.9, 129.6, 131.2, 134.4, 134.9, 136.5, 143.4, 156.0, 159.2, 162.4, 188.6 ppm. MS (ESI): *m/z* 345 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}FO_3$: C, 76.74; H, 3.78 %. Found: C, 76.68; H, 3.77 %.

*7-Hydroxy-10-(2,4-dichlorophenyl)-10H-indeno[1,2-b]chromen-11-one (**4k**)*

IR (KBr, cm^{-1}): 3,437, 2,969, 1,649, 1,597, 1,365, 1,218, 1,202, 1,072, 832; ^1H NMR (500 MHz, DMSO-d_6): δ 4.65 (s, 1H, CH), 6.65 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.82 (dd, $J = 4.1$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.93 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.04–7.09 (m, 2H, Ar–H), 7.30–7.35 (m, 1H, Ar–H), 7.73–7.90 (m, 4H, Ar–H), 9.66 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.0, 104.4, 105.1, 110.7, 124.4, 126.1, 126.5, 128.2, 128.8, 129.4, 131.3, 134.5, 134.9, 136.6, 144.2, 155.8, 158.7, 162.7, 188.8 ppm. MS (ESI): *m/z* 395.9 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{12}Cl_2O_3$: C, 66.85; H, 3.04 %. Found: C, 66.80; H, 3.05 %.

*7-Hydroxy-10-(3,4-dichlorophenyl)-10H-indeno[1,2-b]chromen-11-one (**4l**)*

IR (KBr, cm^{-1}): 3,436, 2,974, 1,649, 1,588, 1,368, 1,222, 1,196, 1,074, 786; ^1H NMR (500 MHz, DMSO-d_6): δ 4.67 (s, 1H, CH), 6.66 (d, $J = 4.2$ Hz, 1H, Ar–H), 6.81 (dd, $J = 4.2$ Hz, $J = 8.0$ Hz, 1H, Ar–H), 6.89 (d, $J = 8.0$ Hz, 1H, Ar–H), 7.12–7.21 (m, 2H, Ar–H), 7.28–7.36 (m, 1H, Ar–H), 7.74–7.89 (m, 4H, Ar–H), 9.68 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.3, 104.0, 105.1, 110.6, 124.6, 125.9, 127.0, 128.2, 128.7, 129.8, 131.0, 134.3, 134.8, 136.6, 144.1, 155.7, 158.5, 163.0, 188.7 ppm. MS (ESI): *m/z* 395.9 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{12}Cl_2O_3$: C, 66.85; H, 3.04 %. Found: C, 66.77; H, 3.00 %.

*7-Hydroxy-10-(3-chlorophenyl)-10H-indeno[1,2-b]chromen-11-one (**4m**)*

IR (KBr, cm^{-1}): 3,435, 2,976, 1,643, 1,590, 1,370, 1,219, 1,194, 1,075, 796; ^1H NMR (500 MHz, DMSO-d_6): δ 4.68 (s, 1H, CH), 6.64 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.82 (dd, $J = 4.1$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.94 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.17–7.31 (m, 4H, Ar–H), 7.70–7.84 (m, 4H, Ar–H), 9.70 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.4, 104.3, 105.2, 110.9, 124.7, 125.8, 126.8, 128.3, 128.9, 129.8, 131.2, 134.3, 134.9, 136.5, 144.2, 155.9, 158.7, 163.1, 188.5 ppm. MS (ESI): 361.45 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}ClO_3$: C, 73.24; H, 3.61 %. Found: C, 73.15; H, 3.59 %.

*7-Hydroxy-10-(3-bromophenyl)-10H-indeno[1,2-b]chromen-11-one (**4n**)*

IR (KBr, cm^{-1}): 3,432, 2,970, 1,645, 1,592, 1,370, 1,217, 1,188, 1,073, 822; ^1H NMR (500 MHz, DMSO-d_6): δ 4.63 (s, 1H, CH), 6.68 (d, $J = 4.1$ Hz, 1H, Ar–H), 6.82 (dd, $J = 4.1$ Hz, $J = 8.2$ Hz, 1H, Ar–H), 6.92 (d, $J = 8.2$ Hz, 1H, Ar–H), 7.21–7.37 (m, 4H, Ar–H), 7.72–7.86 (m, 4H, Ar–H), 9.68 (s, 1H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 30.8, 104.2, 104.9, 111.0, 124.5, 126.4, 126.9, 128.4, 128.9, 129.7, 131.0, 134.6, 135.2, 136.4, 144.0, 155.6, 158.6, 162.7, 188.4 ppm. MS (ESI): *m/z* 405.8 $[M + H]^+$. Anal. Calcd. for $C_{22}H_{13}BrO_3$: C, 65.20; H, 3.21 %. Found: C, 65.15; H, 3.18 %.

General procedure for preparation of 13-phenylindeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one and 12-phenyl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione

A mixture of aldehyde (1 mmol), *β*-naphthol or 2-hydroxynaphthalene-1,4-dione (1 mmol), and 2*H*-indene-1,3-dione (1 mmol) was added to PVPP.OTf (30 mg), and the mixture was stirred at 80 °C in water for an appropriate time. The reaction was monitored by TLC. On completion of the reaction the mixture was diluted with CH_2Cl_2 (20 mL), and filtered to recover the catalyst. The filtrate was then collected and evaporated to dryness to give the crude product, which was purified by silica gel column chromatography with CH_2Cl_2 as mobile phase.

Spectral data for compounds **5a** and **7a**

*13-Phenyl-indeno[1,2-b]naphtho[1,2-e]pyran-12(13H)-one (**5a**)*

IR (KBr, cm^{-1}): 2,988, 1,652, 1,590, 1,366, 1,224, 1,180; ^1H NMR (500 MHz, DMSO-d_6): δ 5.50 (s, 1H, CH), 7.07 (t, $J = 7.4$ Hz, 1H, Ar–H), 7.18 (t, $J = 7.6$ Hz, 2H, Ar–H), 7.26–7.40 (m, 8H, Ar–H), 7.61 (d, $J = 8.8$ Hz, 1H, Ar–H), 7.77–7.89 (m, 3H, Ar–H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 34.0, 111.6, 116.0, 116.8, 117.7, 120.4, 123.8, 125.0, 125.6, 126.6, 127.3, 128.0, 129.1, 130.8, 131.4, 132.0, 132.6, 133.0, 137.2, 143.0, 148.5, 166.7, 192.9; MS (ESI): *m/z* 361 $[M + H]^+$; Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.66 %; H, 4.44 %; Found: C, 86.56 %; H 4.40 %.

*12-Phenyl-12H-indeno[1,2-b]naphtho[3,2-e]pyran-5,11,13-trione (**7a**)*

IR (KBr, cm^{-1}): 3,044, 1,676, 1,660, 1,642; ^1H NMR (500 MHz, DMSO-d_6): δ 5.38 (s, 1H, CH), 7.24–7.49 (m, 6H, Ar–H), 7.66–7.88 (m, 4H, Ar–H), 7.94 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.08 (d, $J = 7.6$ Hz, 1H, Ar–H), 8.22 (d, $J = 7.6$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 38.9, 102.3, 120.6, 123.4, 123.7, 126.4, 126.8, 127.7, 128.2, 128.5, 130.6, 131.6, 134.4, 135.1, 136.3, 137.7, 144.4, 161.0, 172.0, 178.2, 182.6, 190.9 ppm. MS (ESI): *m/z* 391 $[M + H]^+$; Anal. Calcd for $C_{26}H_{14}O_4$: C, 79.99; H, 3.61 %; Found: C, 79.86 %; H, 3.57 %.

Results and discussion

In this paper we report a very efficient one-pot, three-component synthesis of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one derivatives catalyzed by PVPP.OTf. To optimize the reaction conditions, we chose the condensation of 4-chlorobenzaldehyde (1 mmol), resorcinol (1 mmol), and 2*H*-indene-1,3-dione (1 mmol), catalyzed by PVPP.OTf under different conditions, as model reaction. The results are summarized in Table 1. The effect of solvent, temperature, and amount of catalyst was examined.

Several different solvents (methanol, ethanol, toluene, dichloromethane, tetrahydrofuran, acetonitrile and water) were screened in the model reaction (Table 1, entries 1–7). The results suggested that a good yield was obtained in water (Table 1, entry 7). To determine the effect of temperature on the model reaction, we studied the effect of different temperatures (room temperature, 50, 60, 70, 80, and 90 °C; Table 1, entries 7–12). As shown in Table 1, when the reaction temperature was varied from room temperature to 80 °C product yield gradually increased, with the highest yield being obtained at 80 °C, i.e. product yield was not affected by further increasing the reaction temperature. To optimize catalyst loading the model reaction was performed with 0, 10, 20, 30, and 40 mg PVPP.OTf at 80 °C in water (Table 1, entries 7 and 13–16). Thirty milligrams of PVPP.OTf was found to be sufficient to promote the reaction; larger amounts of the catalyst did not lead to any significant improvement in product yield. It should be mentioned that when the reaction was

Table 1 Synthesis of 7-hydroxy-10-(4-chlorophenyl)-10*H*-indeno[1,2-*b*]chromen-11-one in the presence of the PVPP.OTf catalyst under different reaction conditions

Entry	Solvent	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)[a]
1	MeOH	30	Reflux	120	70
2	EtOH	30	Reflux	120	77
3	Toluene	30	Reflux	120	61
4	CH_2Cl_2	30	Reflux	150	49
5	THF	30	Reflux	150	37
6	CH_3CN	30	Reflux	150	45
7	Water	30	80	75	94
8	Water	30	RT	180	44
9	Water	30	50	150	57
10	Water	30	60	120	75
11	Water	30	70	90	84
12	Water	30	90	75	94
13	Water	0	80	240	–
14	Water	10	80	120	48
15	Water	20	80	90	73
16	Water	40	80	75	94

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), resorcinol (1 mmol), 2*H*-indene-1,3-dione (1 mmol)

[a] Isolated yield

performed in the absence of catalyst over a long period of time (240 min) at 80 °C in water, no yield of the product was obtained.

With these optimized conditions we proceeded to investigate the general scope and applicability of this method with a variety of simple and readily available aldehydes (Table 2). A wide range of aromatic aldehydes containing electron-withdrawing (i.e., Cl, Br, and NO_2) or electron-donating (i.e., CH_3 and OCH_3) groups at the *ortho*, *meta*, or *para* position of the benzene ring were readily converted into the corresponding 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-ones in good to excellent isolated yields with short reaction times under the optimized conditions (Table 2, entries 1–14). Aromatic aldehydes with electron-donating groups required longer reaction times and led to lower yields than those with electron-withdrawing groups.

Inspired by the catalytic potential of PVPP.OTf, we extended the procedure by using *β*-naphthol or 2-hydroxynaphthalene-1,4-dione instead of resorcinol. Condensation of benzaldehyde, *β*-naphthol or 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione was conducted under similar reaction conditions. The desired products, 13-phenylindeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one (**5a**) and 12-phenyl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione (**7a**), were obtained in 91 and 90 % yield, respectively (Table 3).

The reusability of the catalyst was evaluated. Briefly, the model reaction was studied under the optimized reaction conditions. On completion of the reactions the

Table 2 Synthesis of a variety of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one derivatives

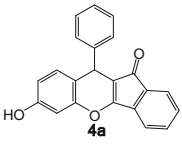
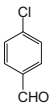
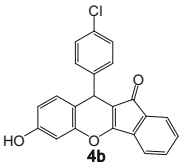
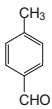
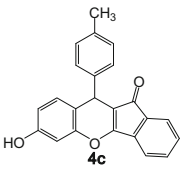
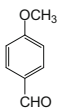
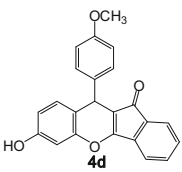
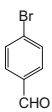
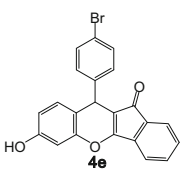
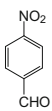
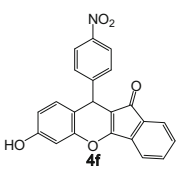
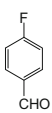
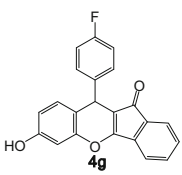
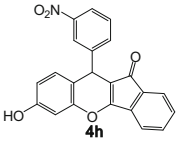
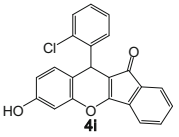
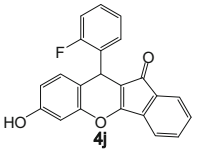
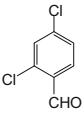
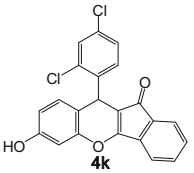
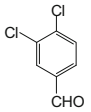
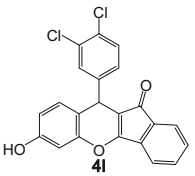
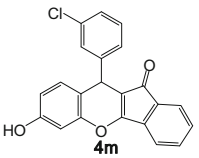
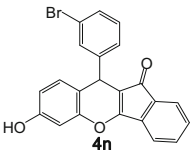
Entry	Aldehydes	Product	Time (min)	Yield (%)[b]	Mp (°C)
1		 **4a**	80	92	245 – 247
2		 **4b**	75	94	219 – 220
3		 **4c**	90	89	201 – 202
4		 **4d**	90	90	211 – 213
5		 **4e**	70	94	208 – 210
6		 **4f**	70	94	233 – 235
7		 **4g**	65	95	199 – 200

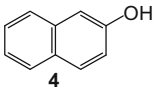
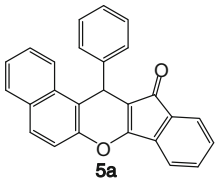
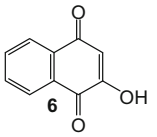
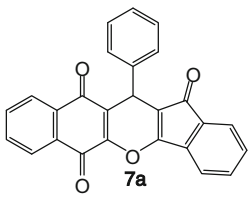
Table 2 continued

Entry	Aldehydes	Product	Time (min)	Yield (%)[b]	Mp (°C)
8			75	93	214 – 216
9			75	90	247 – 248
10			75	91	223 – 225
11			75	90	206 – 208
12			75	91	231 – 232
13			70	92	212 – 214
14			65	93	244 – 245

Reaction conditions: aldehydes (1 mmol), resorcinol (1 mmol) and 2*H*-indene-1,3-dione (1 mmol) heating at 80 °C in the presence of PVPP.OTf (30 mg) in water

[a] Isolated yields

Table 3 Reaction of benzaldehyde, *β*-naphthol or 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione for synthesis of 13-phenylindeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one and 12-phenyl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione

Entry	Hydroxy compound	Product	Time (min)	Yield (%)[b]	Mp (°C)
1	 **4**	 **5a**	30	91	245 – 247
2	 **6**	 **7a**	35	90	311 – 313

Reaction conditions: aldehydes (1 mmol), hydroxy compound (1 mmol) and 2*H*-indene-1,3-dione (1 mmol) heating at 80 °C in the presence of PVPP.OTf (30 mg) in water

[a] Isolated yields

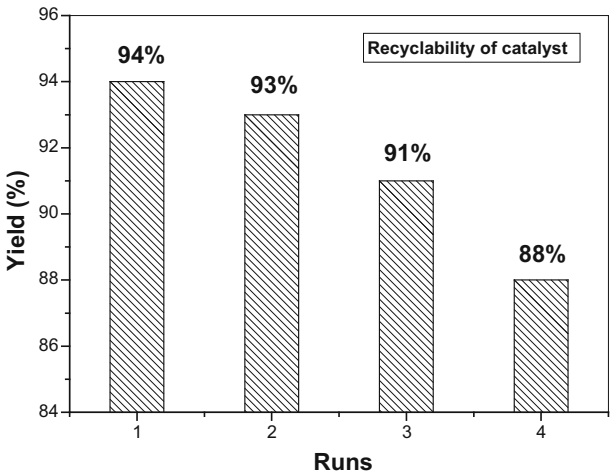
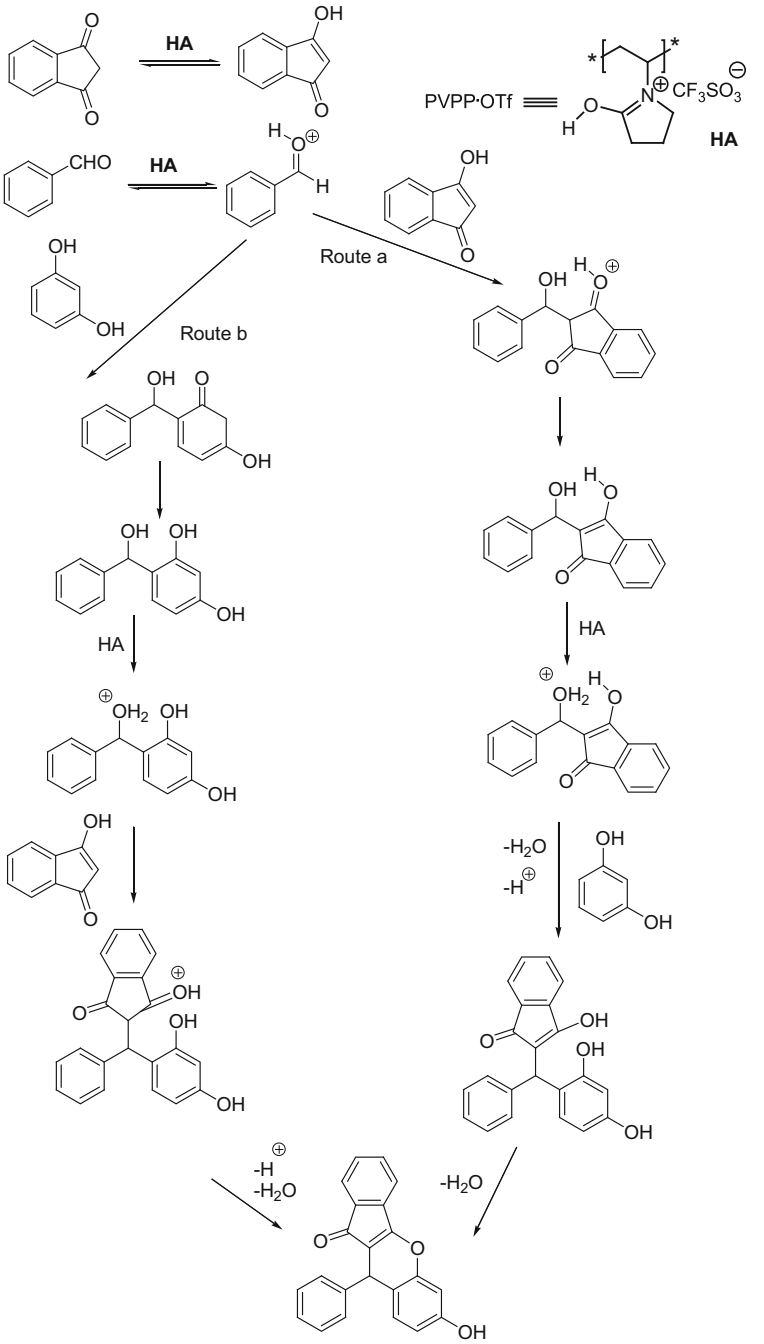


Fig. 1 Recyclability of the catalyst PVPP.OTf in the synthesis of 7-hydroxy-10-(4-chlorophenyl)-10*H*-indeno[1,2-*b*]chromen-11-one in water at 80 °C

catalyst was separated by filtration, washed with diethyl ether, dried under vacuum, and used again in the same reaction. This process was repeated over four runs and the results showed that the reactions proceeded efficiently to give the desired



Scheme 3 Possible mechanism of formation of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one

products without any significant changes in yield of the products. As shown in Fig. 1, the solid acid PVPP.OTf can be recycled at least four times without significant decrease in catalytic activity; the yields ranged from 94 to 88 %.

A rational mechanism showing the probable sequence of events in the formation of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-ones with PVPP.OTf as catalyst is given in Scheme 3. The reaction could proceed via two different routes, i.e., routes a and b.

Conclusions

In summary, we have shown that PVPP.OTf is an efficient solid-acid catalyst for synthesis of 7-hydroxy-10-aryl-10*H*-indeno[1,2-*b*]chromen-11-one derivatives by condensation of aldehydes with resorcinol and 2*H*-indene-1,3-dione at 80 °C in water. We also synthesized 13-phenylindeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one and 12-phenyl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione by condensation of benzaldehyde, *β*-naphthol or 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione with PVPP.OTf as catalyst. The non-hazardous experimental conditions, reusable catalyst, ease of reaction, short reaction times, high yields, and metal-free catalyst are notable advantages of this procedure. It is, thus, a better and more practical alternative to existing methods.

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