Res Chem Intermed
DOI 10.1007/s11164-013-1521-5

Polyvinylpolypyrrolidone supported triflic acid (PVPP.OTf); an efficient and recyclable heterogeneous catalyst for one-pot condensation of β-naphthol, aldehydes, and cyclic 1,3-dicarbonyl compounds

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Received: 19 August 2013 / Accepted: 18 December 2013

Abstract Polyvinylpolypyrrolidoniume triflate (PVPP.OTf) is found to be a recyclable heterogeneous catalyst for the one-pot condensation of β-naphthol, aldehydes, and cyclic 1,3-dicarbonyl compounds in good to excellent yield under reflux conditions. These catalytic condensations have advantages from the viewpoint of green chemistry. PVPP.OTf catalyst is air-stable, cost-effective, easy to handle, easily separated from reaction products, and recovered in excellent purity for direct reuse.

Keywords Polyvinylpolypyrrolidoniume triflate · Heterogeneous · Benzoxanthene · β-Naphthol

Introduction

Xanthene and their structural analogues are significant for their pharmacological activities. They show a wide spectrum of biological activities such as anti-inflammatory [1], antiviral [2], and antibacterial [3], and can be utilized as antagonists for drug-resistant leukemia lines [4]. In addition, they have also been used as dyes [5, 6] and pH-sensitive fluorescent materials [7, 8], as well as in laser technologies [9, 10]. Moreover, several polycyclic compounds containing the xanthene skeleton have been isolated from natural sources [11]. Consequently, wide demands of diverse xanthene derivatives in various fields have promoted the development of practical and diversified synthetic methods. Recently, several elegant multicomponent strategies for the synthesis of tetrahydrobenzo[*a*]xanthen-11-one derivatives by the cyclocondensation of naphthols, aldehydes, and 1,3-diketones utilizing different types of catalysts have been reported [12–17]. These

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Published online: 07 January 2014

methods show varying degrees of successes as well as limitations, such as harsh reaction conditions, expensive and detrimental metal reagents, tedious work-up, low product yields, long reaction times, and co-occurrence of several side products. Considering the above reports, the development of novel methods for the synthesis of xanthenes is of great importance because of their potential biological and pharmaceutical activities.

In recent years, polymer-supported reagents are gaining considerable attention because polymeric reagents facilitate work-up and product purification, reduce environmental damage, and have easy separation, which make them promising for both academic and industrial applications [18]. Triflic acid (TfOH) is widely used as a homogeneous acid catalyst due to its very strong Brønsted acidity ($pK_a = -13.6$), and its structure and properties [19–23]. However, TfOH is highly corrosive and is a fuming liquid, and so there are difficulties involved in storage, transportation, handling and waste disposal, thus severely restricting its application in industry. Despite its widespread use in acid-catalyzed reactions, these drawbacks, together with product isolation, catalyst recovery, and toxicological concerns, still exist. The immobilization of TfOH onto solid supports affords solid acids which can be easily handled, as they are invariably of low toxicity, and are non-corrosive, free-flowing powders with superior thermal and mechanical stability under catalytic conditions. Thus, some immobilization processes for TfOH on solid supports have been designed [24–27]. In continuing our studies on the application of new reagents or systems for organic functional group transformations [28–30], we describe the preparation of polyvinylpolypyrrolidone-supported TfOH (PVPP.OTf) and its application as a catalyst for the synthesis of xanthene derivatives. In this light, we have supported TfOH on polyvinylpolypyrrolidone to prepare an efficient, mild catalyst for the heterogeneous preparation of tetrahydrobenzo[*a*]xanthen-11-one derivatives (Scheme 1).

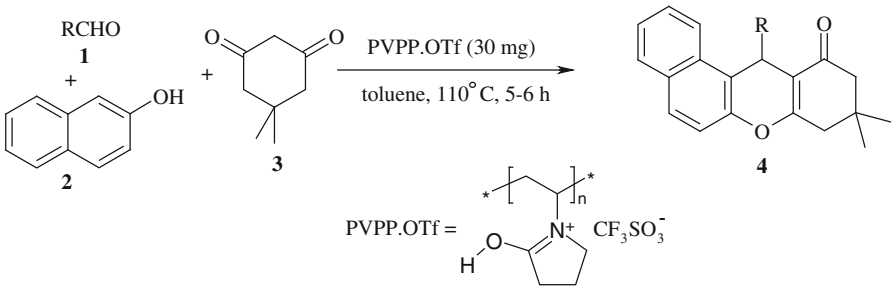
Experimental

Apparatus and analysis

NMR spectra were determined on an FT-NMR Bruker AV-400 spectrometer in $CDCl_3$ or DMSO-d_6 and are expressed in d values relative to tetramethylsilane; coupling constants (J) are measured in Hz. Melting points were determined on an Electrothermal 9100 apparatus. Infrared spectra were recorded on a Rayleigh WQF-510 Fourier transform instrument. Commercially available reagents were used throughout without further purification.

Preparation of the Polyvinylpolypyrrolidoniume triflate (PVPP.OTf)

To a suspension of polyvinylpolypyrrolidone (3.0 g) in toluene (35 mL), TfOH (2.0 g, 13 mmol) was added. The mixture was stirred magnetically for 60 min at r.t. The toluene was removed under reduced pressure and the residue was dried at



Scheme 1 Reaction of β-naphthol, benzaldehyde, and 5,5-dimethylcyclohexane1,3-dione

110 °C for 2 h to afford PVPP.OTf as a white powder. The number of H^+ sites PVPP.OTf determined by acid–base titration was 10 mequiv./g.

General procedure for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivative

A toluene solution (3 mL) of aldehyde (1 mmol), β-naphthol (1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1 mmol) was mixed with PVPP.OTf (30 mg), and the mixture was stirred at 110 °C for an appropriate time. The reaction was monitored by TLC. After completion of the reaction, the mixture was washed with chloroform and filtered to recover the catalyst. The filtrate was evaporated and dried. Products were characterized by comparison of their physical and spectral data with those of authentic samples [22]. Spectroscopic data for selected examples are shown below. Spectroscopic data for selected examples as follows:

*12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**4a**)*

White solid; mp 180–182 °C; IR (KBr, cm^{-1}): 3,070, 2,935, 1,640, 1,368. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J = 8.2$ Hz, 1H), 7.75–7.80 (m, 2H), 7.10–7.42 (m, 7H), 5.65 (s, 1H), 2.56 (s, 2H), 2.33 (d, $J = 16.1$ Hz, 1H), 2.25 (d, $J = 16.1$ Hz, 1H), 1.12 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.7$, 164.1, 152.1, 147.2, 146.3, 132.1, 130.3, 129.2, 129.2, 128.3, 127.1, 125.1, 123.3, 123.0, 116.4, 115.3, 113.1, 50.3, 41.5, 34.7, 31.9, 29.3, 27.2.

*12-(2-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**4b**)*

White solid; mp 178–180 °C; IR(KBr, cm^{-1}): 3,070, 2,929, 1,645, 1,369, 1,230, 1,180. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.22$ (d, $J = 8.3$ Hz, 1H), 7.71–7.75 (m, 2H), 7.27–7.49 (m, 5H), 6.95–7.07 (m, 2H), 5.88 (s, 1H), 2.60 (s, 2H), 2.35 (d, $J = 16.0$ Hz, 1H), 2.24 (d, $J = 16.0$ Hz, 1H), 1.12 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.5$, 164.2, 148.1, 142.5, 133.0, 131.3,

131.5,131.2,129.5,129.0,128.1,127.2,127.0,126.5,124.9, 122.9,117.2,117.0, 114.1, 50.7, 41.4, 32.8, 32.1, 29.4, 27.1.

*12-(3-Chlorophenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (**4c**): entry 6*

White solid; mp 175–177 °C; IR(KBr, cm^{-1}): 3,050, 2,927, 1,647, 1,365. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 8.2$ Hz, 1H), 7.88–8.01 (m, 2H), 7.40–7.50 (m, 3H), 7.36 (s, 1H), 7.19 (d, $J = 4.4$ Hz, 2H), 7.11 (s, 1H), 5.60 (s, 1H), 2.60 (s, 2H), 2.30 (d, $J = 16.2$ Hz, 1H), 2.13 (d, $J = 16.2$ Hz, 1H), 1.11 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 195.7$, 164.0, 148.3, 148.0, 134.5, 132.1, 131.3, 130.8, 130.3, 129.2, 128.8, 128.1, 127.5, 127.1, 125.9, 124.1, 117.9, 117.3, 113.4, 51.9, 42.0, 35.7, 33.7, 29.8, 26.9.

*12-(4-Nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (**4d**)*

White solid; mp 177–180 °C; IR(KBr, cm^{-1}): 3,078, 2,933, 2,911, 1,645, 1,595, 1,510, 1,375, 1,347. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 8.4$ Hz, 2H), 7.78–7.80 (m, 3H), 7.32–7.51 (m, 5H), 5.80 (s, 1H), 2.60 (s, 2H), 2.35 (d, $J = 16.3$ Hz, 1H), 2.24 (d, $J = 16.3$ Hz, 1H), 1.11 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.2$, 165.1, 51.6, 147.5, 145.9, 131.4, 130.9, 129.6, 129.3, 128.4, 127.1, 125.2, 123.2, 122.9, 117.3, 115.9, 113.0, 50.7, 41.2, 34.6, 32.1, 29.3, 27.1.

*12-(3-Nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (**4e**)*

White solid; mp 168–170 °C; IR (KBr, cm^{-1}): 3,073, 2,950, 1,648, 1,527, 1,370, 1,352. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.09$ (s, 1H), 7.79–7.94 (m, 5H), 7.35–7.46 (m, 4H), 5.80 (s, 1H), 2.60 (s, 2H), 2.36 (d, $J = 16.2$ Hz, 1H), 2.27 (d, $J = 16.2$ Hz, 1H), 1.14 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.4$, 164.2, 148.5, 147.7, 146.5, 134.5, 132.1, 130.6, 129.6, 129.1, 128.4, 127.2, 125.0, 123.2, 123.0, 121.2, 117.2, 115.6, 113.2, 51.2, 41.4, 34.5, 32.1, 29.1, 27.3.

*12-(4-Fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**4f**)*

White solid, m.p. 184–185 °C; IR (KBr, cm^{-1}): 3,034, 2,952, 2,880, 1,654, 1,620, 1,508. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (d, $J = 8.4$ Hz, 1H), 7.76 (t, $J = 8.2$ Hz, 2H), 7.30–7.45 (m, 5H), 6.86 (t, $J = 8.6$ Hz, 2H), 5.72 (s, 1H), 2.55 (s, 2H), 2.24 (d, $J = 16.4$ Hz, 1H), 2.31 (d, $J = 16.4$ Hz, 1H), 1.13 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.8$, 163.6, 148.1, 141.6, 132.5, 131.7, 129.9, 129.2, 128.5, 127.2, 125.1, 123.5, 117.3, 117.2, 115.3, 114.9, 114.2, 51.2, 41.4, 34.3, 32.2, 29.2, 27.2.

*12-(4-Bromophenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (**4g**)*

White solid; mp 186–187 °C; IR (KBr, cm^{-1}): 3,072, 2,936, 1,643, 1,371.^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.88$ (d, $J = 8.3$ Hz, 1H), 7.76–7.80 (m, 2H), 7.38–7.45 (m, 2H), 7.26–7.33 (m, 3H), 7.20–7.23 (m, 2H), 5.66 (s, 1H), 2.56 (s, 2H), 2.31 (d, $J = 16.3$ Hz, 1H), 2.24 (d, $J = 16.3$ Hz, 1H), 1.13 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.8, 164.0, 147.7, 143.8, 131.5, 131.2, 131.2, 130.1, 129.2, 128.5, 127.1, 125.0, 123.4, 120.1, 117.1, 116.9, 113.7, 50.8, 41.4, 34.2, 32.3, 29.4, 27.1$.

*12-(2-Bromorophenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11 (12H)-one (**4h**)*

White solid; mp 168–170 °C; IR (KBr, cm^{-1}): 3,069, 2,933, 1,646, 1,377.^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.12$ (d, $J = 16.1$ Hz, 1H), 7.88–7.91(m, 2H), 7.46–7.52 (m, 2H), 7.40–7.42(m, 2H), 7.18–7.21 (m, 2H), 6.97–7.01 (m, 1H), 5.75 (s, 1H), 2.71 (s, 2H), 2.32 (d, $J = 16.1$ Hz, 3H), 2.08 (d, $J = 16.1$ Hz, 1H), 1.06 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.1, 163.3, 146.6, 142.1, 132.2, 131.2, 131.5, 131.2, 129.5, 129.0, 128.3, 127.5, 127.1, 126.6, 124.1, 123.9,116.3, 117.1, 113.2, 50.5, 41.4, 33.1, 32.1, 29.1, 27.1$.

*12-Phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-one (**4i**)*

White solid; mp 150–152 °C; IR (KBr, cm^{-1}): 3,055, 2,950, 2,879, 1,650, 1,376. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, $J = 8.1$ Hz, 1H), 7.73–7.78 (m, 2H),7.05–7.40 (m, 8H), 5.73 (s, 1H), 2.61 (s, 2H), 2.33 (d, $J = 16.1$ Hz, 1H), 2.25 (d, $J = 16.1$ Hz, 1H), 1.12 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.6, 164.1, 147.5, 144.3, 132.1, 131.3, 128.8, 128.4, 128.2, 128.0, 126.6, 126.1, 124.8, 123.5, 117.3, 117.1, 114.1, 50.5, 41.5, 34.7, 32.3, 29.6, 27.2$.

*12-(4-Methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**4j**)*

White solid; mp 205–206 °C; IR (KBr, cm^{-1}): 3,056, 2,948, 1,642, 1,224, 1,170. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, $J = 8.1$ Hz, 1H), 7.71–7.76 (m, 2H), 7.21–7.42 (m, 5H), 6.71 (d, $J = 8.2$ Hz, 2H), 5.64 (s, 1H), 3.68 (s, 3H), 2.56 (s, 2H), 2.35 (d, $J = 16.2$ Hz, 1H), 2.27 (d, $J = 16.2$ Hz, 1H), 1.13 (s, 3H), 0.98 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.5, 164.1, 155.7, 146.3, 136.1,133.6, 130.6, 130.2, 128.5, 127.2, 126.5, 125.1, 123.6, 122.4, 117.1, 116.8, 115.4, 113.3, 112.7, 53.4, 49.7, 40.2, 32.6, 31.1, 28.4, 26.1$.

*12-(4-Methylphenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (**4k**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.0$ (d, $J = 8.4$ Hz, 1H), 7.33–7.77 (m, 2H), 7.40–7.44 (m, 1H), 7.32–7.37 (m, 2H), 7.20–7.30 (m, 2H), 6.96 (d, $J = 8.0$ Hz,

2H), 5.66 (s, 1H), 2.54 (s, 2H), 2.30 (d, $J = 16.2$ Hz, 1H), 2.22 (d, $J = 16.2$ Hz, 1H), 2.19 (s, 3H), 1.11 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.8$, 163.7, 147.6, 141.8, 135.6, 131.5, 131.4, 128.9, 128.6, 128.3, 128.3, 126.9, 124.8, 123.6, 117.9, 117.1,114.4, 50.9, 41.5, 34.2, 32.5, 29.3, 27.2, 20.9.

*12-(3,4-dimethylphenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11 (12H)-one (**4l**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.02$ (d, $J = 8.5$ Hz, 1H), 7.77–7.72 (m, 2H), 7.42–7.25 (m, 3H), 7.11–7.04 (m, 2H), 6.91 (d, $J = 8.0$ Hz, 1 H), 5.63 (s, 1H), 2.56 (s, 2H), 2.26 (dd, $J_1 = 4.0$ Hz, $J_2 = 16.0$ Hz, 2H), 2.13 (s, 3H), 2.09 (s, 3H), 1.11 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 195.2, 164.1, 147.6, 142.1, 135.2, 134.4, 132.5, 129.7, 129.3, 128.7, 128.4, 127.1, 125.6, 124.9, 123.5, 117.8, 117.1, 114.5, 52.1, 42.4, 34.3, 32.6, 29.2, 26.4, 21.1, 19.2.

*12-(3-Hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (**4m**)*

White solid; mp 239–240 °C; IR (KBr, cm^{-1}): 3,410, 3,050, 2,960, 1,642, 1,590, 1,370, 1,225, 1,70. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, $J = 8.1$ Hz, 1H), 7.73–7.79 (m, 2H),7.30–7.44 (m, 3H), 7.03 (t, $J = 7.7$ Hz, 1H), 6.95 (s, 1H), 6.81 (d, $J = 7.5$ Hz, 1H), 6.58 (d, $J = 6.1$ Hz, 1H), 5.67 (s, 1H), 5.45 (s, 1H), 2.55 (s, 2H), 2.36 (d, $J = 16.1$ Hz, 1H), 2.31 (d, $J = 16.1$ Hz, 1H), 1.12 (s, 3H), 0.98(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.2$, 164.6, 148.2, 147.1, 146.3, 135.15, 131.4, 130.6, 129.5, 129.2,128.1,127.1, 126.1,123.2, 123.0, 120.7,117.3, 115.5, 113.2, 50.6, 42.0, 34.7, 32.1, 29.1, 27.1.

*9,9-Dimethyl-12-styryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-one (**4n**)*

White solid; mp 149–150 °C; IR (KBr, cm^{-1}): 3,078, 2,930, 1,646, 1,465, 1,382. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.04$ (d, $J = 8.3$ Hz, 1H), 7.74–7.83 (m, 2H), 7.18–7.50 (m, 8H), 6.43–6.46 (m, 1H), 6.18 (d, $J = 15.8$ Hz, 1H), 5.35 (d, $J = 6.3$ Hz, 1H), 2.55 (s, 2H), 2.37 (s, 2H), 1.06 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.2$, 165.1, 147.7, 137.1, 131.4, 130.8, 130.3, 128.7, 128.3, 128.0, 127.4, 127.0, 126.1, 125.1, 123.6, 117.1, 113.1, 51.1, 41.4, 32.4, 31.3, 29.1, 27.4.

Results and discussion

In order to optimize the reaction conditions, we chose the condensation of the reaction of β-naphthol, 4-chlorobenzaldehyde, and dimedone catalyzed by PVPP.OTf under different conditions both in the absence and the presence of PVPP.OTf, and results are given in Table 1. Then, the effect of temperature, the amount of catalyst, and the reaction time on the yield of the product were examined. It was found that this condensation reaction was affected by various solvents

(Table 1, entries 2–11). Among them, toluene provided the highest yield at refluxed temperature after 5 h (Table 1, entry 5). In addition, no conversion to the product was obtained in the absence of the catalyst even after 10 h (Table 1, entry 1). Next, we examined the optimal amount of catalyst using the same model reaction. We observed that 30 mg PVPP.OTf was sufficient to catalyze the reaction smoothly. Increasing either the amount of the catalyst and/or prolonging the reaction time did not improve the yield (Table 1, entry 11), while reducing these factors led to a reduction in product yield (Table 1, entries 3, 4). Surprisingly, when the reaction was carried out in toluene medium, solid product was separated at the end of the reaction.

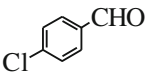
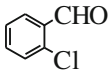
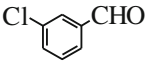
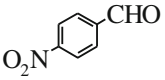
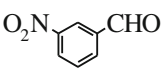
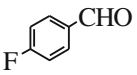
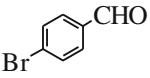
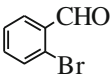
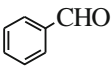
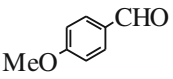
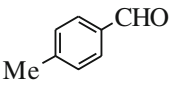
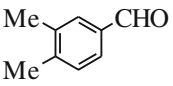
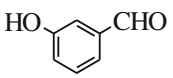
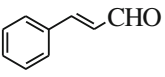
Using these optimized reaction conditions, the scope and efficiency of this approach was explored for the synthesis of a wide variety of substituted benzo[*a*]xanthenes and results are summarized in Table 2. A wide range of structurally varied aldehyde reacted smoothly and quickly to give the corresponding benzo[*a*]xanthenes in high yield and purity as listed in the table 2. In all cases, aromatic aldehydes substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave the products in good yields.

It could also be concluded that the aldehydes bearing electron-withdrawing groups required shorter times and gave higher yields (Table 2, entries 1–8). In addition, α,β-unsaturated aldehyde also afforded good yields (Table 2, entry 14). In most cases, no undesired side products such as aryl-14*H*-dibenzo[*a*,*j*]xanthene were obtained under these conditions [15]. However, the reaction failed with aliphatic aldehydes such as propionaldehyde and cyclohexanecarbaldehyde (Scheme 2). In these cases, alkyl-14*H*-dibenzo[*a*,*j*]xanthene, **5a**, **b**, was the exclusive product. Another important feature of this procedure is the survival of a variety of functional groups such as ethers, alkyls, nitros, and halides under the present reaction conditions.

Table 1 Effect of different PVPP.OTf and solvent on formation of **4**

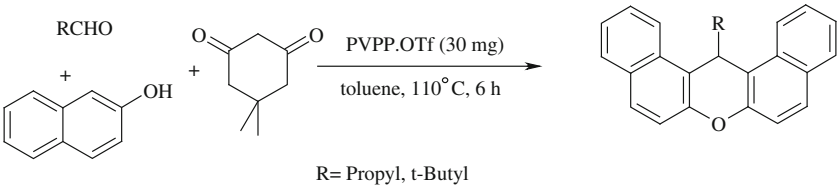
Entry	PVPP.OTf amount (mg)	Condition/solvent	Time (h)/yield
1	0	r.t./toluene	24/0
2	20	r.t./toluene	10/60
3	10	Reflux/toluene	10/60
4	20	Reflux/toluene	8/90
5	30	Reflux/toluene	5/95
6	30	r.t./CH_2Cl_2	12/30
7	30	r.t./THF	12/20
8	30	r.t./ethanol	10/60
9	30	r.t./H_2O	24/10
10	30	r.t./diethyl ether	24/10
11	50	Reflux/toluene	5/95

Table 2 Synthesis of benzo[*a*]xanthenes in the presence of PVPP.OTf

Entry	Aldehyde	Product	Time (h)	Yield %
1		**4a**	5	95
2		**4b**	6	90
3		**4c**	5	90
4		**4d**	5	90
5		**4e**	5	85
6		**4f**	5	92
7		**4g**	5	90
8		**4h**	5	85
9		**4i**	5	85
10		**4j**	6	85
11		**4k**	6	85
12		**4l**	6	80
13		**4m**	6	85
14		**4n**	5	85

Characterizing the Brønsted acid sites presented on the polymer was performed by recording the FT-IR spectrum of PVPP.OTf, which shows a strong broad absorption at 3,432 cm^{-1} for the O–H bonds and a moderate absorption at 1,648 cm^{-1} corresponding to the imine group on the backbone (Fig. 1). Respectively [31], the bands at 1,225 and 1,174 cm^{-1} were assigned to the S=O asymmetric and symmetric stretching vibrations of the $–SO_3^-$ group. The loading capacity of the reagent was determined by titration and found to be 10 mmol/g, whereas its silica-supported analogue has a loading capacity of less than 1 mmol/g.

As PVPP.OTf is not soluble in toluene, no PVPP.OTf leaching as well as no contribution of homogeneous catalysis in the course of reaction were expected. To prove this, after 3 h, the catalyst was removed from the toluene by filtration and the supernatant was tested for activity. No activity was observed, indicating that there was no contribution of homogeneous catalysis in this reaction. After the reaction, the catalyst can be easily separated (by filtration) and reused after washing with dichloromethane with gradual decrease in its activity. For example, the reaction of β-naphthol, 4-chlorobenzaldehyde, and dimedone afforded the corresponding xanthene derivative in 95, 95, and 90 % isolated yield over three cycles.



Scheme 2 Reaction of β-naphthol, aliphatic aldehyde, and 5,5-dimethylcyclohexane1,3-dione

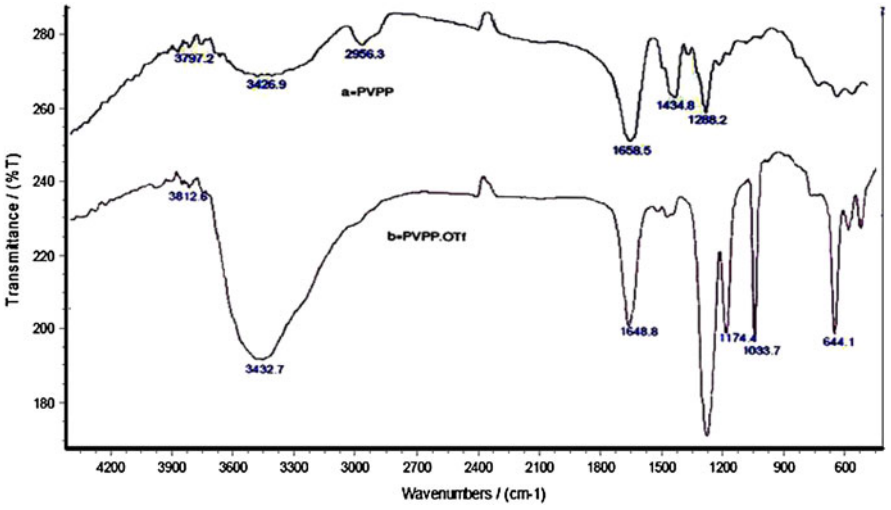


Fig. 1 The FT-IR spectrum of the polyvinylpolypyrrolidone (PVPP) and (PVPP.OTf) catalyst

Conclusion

In conclusion, we have developed an efficient synthesis of tetrahydrobenzo[*a*]xanthen-11-one derivatives via one-pot condensation of β-naphthol, aldehydes, and cyclic 1,3-dicarbonyl compounds in the present of polyvinylpolypyrrolidoniume triflate. In contrast to the existing methods using potentially hazardous catalysts/additives, the present method offers the following competitive advantages: (1) PVPP.OTf is easy to prepare from commercially available polyvinylpolypyrrolidone and TfOH, (2) short reaction time, (3) ease of product isolation/purification by non-aqueous work-up, (4) no side reaction, (5) low costs and simplicity in process and handling, and (6) tetrahydrobenzo[*a*]xanthen-11-one is produced by an environmentally benign process.

Acknowledgment This research is supported by the Islamic Azad University, Ayatollah Amoli Branch.

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