

SOLVENT-FREE SYNTHESIS OF XANTHENE DERIVATIVES BY PREYSSLER TYPE HETEROPOLYACID

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ABSTRACT. Dimedone reacted with aromatic aldehydes and 3,4-methylenedioxyphenol or β -naphthol in the presence of a catalytic amount of Preyssler type heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$, as a green and reusable catalyst under solvent-free conditions to form a variety of new xanthene derivatives in very good yields.

KEY WORDS: Xanthene derivatives, Solvent-free synthesis, Preyssler type heteropolyacid, 3,4-Methylene dioxyphehol, β -Naphthol, Three-component one-pot reactions

INTRODUCTION

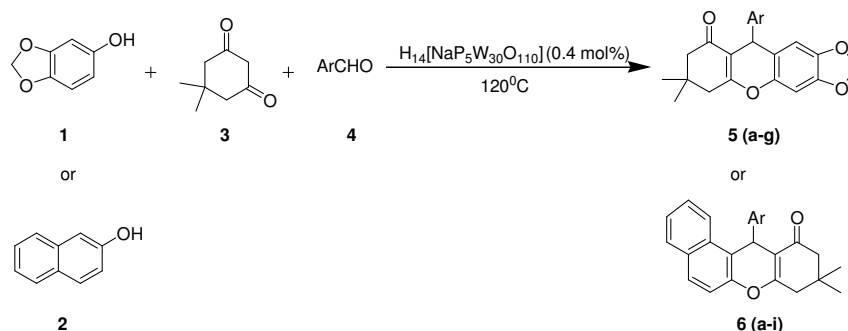
Multi-component reactions (MCRs) have emerged as an important tool for building of diverse and complex organic molecules through carbon-carbon and carbon-heteroatom bond formations taking place in tandem manner [1]. Particularly, in the last three decades a number of three and four-component reactions have been developed [2].

Xanthene derivatives are very important heterocyclic compounds and have been widely used as dyes fluorescent materials for visualization of bio-molecules and laser technologies due to their useful spectroscopic properties [3]. They have also been reported for their agricultural bactericide activity [4], photodynamic therapy [5], anti-inflammatory effect [6] and antiviral activity [7]. Due to their wide range of applications, these compounds have received a great deal of attention in connection with their synthesis. A number of methods have been developed for the preparation of the xanthenes [8-10]. Due to the importance of these compounds, we became interested in constructing a library based on 10-aryl-7,7-dimethyl-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-*b*]xanthen-9-ones and 12-aryl-9,9-dimethyl-8,9,10,12-tetrahydro-11H-benzo[*a*]xanthen-11-ones.

The use of heteropolyacids (HPAs) has recently received considerable attention as non-toxic, eco-friendly and environmentally benign catalysts for various organic transformations to afford the corresponding products in good yields. Due to the numerous advantages associated with these eco-friendly and green catalysts [11-16], HPAs and their salts have been explored as powerful, efficient and eco-friendly catalysts in organic reactions such as liquid phase bromination of phenol [17], chemoselective oxathioacetalization of carbonyl compounds [18], Fries rearrangement of aryl esters [19], isomerization of *n*-hexane [20], alkylation of *p*-cresol with *tert*-butanol [21].

We have been interested in the synthesis of heterocyclic systems [22] and application of heteropolyacids in organic synthesis [23-25]. In this article, we wish to report a facile condensation of 3,4-methylenedioxyphenol (**1**) or β -naphthol (**2**), 5,5-dimethyl-1,3-cyclohexanedione (dimedone, **3**), aromatic aldehydes (**4**) and in the presence of a catalytic amount of Preyssler type heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$, to produce a variety of xanthene derivatives (**5** and **6**) in excellent yields (Scheme 1).

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EXPERIMENTAL

General

Melting points were measured by using the capillary tube method with a Bamstead electro thermal 9200 apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker AQS 500-AVANCE spectrometer at 500 and 125 MHz, respectively, using TMS as an internal standard (DMSO solution). IR spectra were recorded from KBr disk on the FT-IR Bruker Tensor 27. The reactions were monitored by TLC. Elemental analyses were done on 2400-SERIES, Perkin Elmer Company analyzer. All the solvents and reagents were purchased from Aldrich and Merck with high-grade quality and used without any purification. All the products were characterized by their spectra and physical data.

Table 1. Synthesis of **5a-g** in the presence of a catalytic amount of $\text{H}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}$.

Entry	Ar	Time (h)	Product	Yield (%) ^a	M.p. (°C)
1	C_6H_5	2	5a	88	190-192
2	2,4- $\text{Cl}_2\text{C}_6\text{H}_3$	1.3	5b	90	214-215
3	2- $\text{CH}_3\text{C}_6\text{H}_4$	1.6	5c	88	176-178
4	3- $\text{NO}_2\text{C}_6\text{H}_4$	2	5d	87	156-158
5	4- $\text{NO}_2\text{C}_6\text{H}_4$	1.3	5e	86	201-202
6	3- $\text{CH}_3\text{OC}_6\text{H}_4$	1.5	5f	90	141-142
7	4- $\text{CH}_3\text{OC}_6\text{H}_4$	1.6	5g	85	197-198

^a Yields are related to isolated pure products.

Table 2. Synthesis of **6a-i** in the presence of a catalytic amount of $\text{H}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}$.

Entry	Ar	Product	Time (h)	Yield (%) ^a	M.p. (°C)
1	4- BrC_6H_4	6a	1.5	89	186-188
2	4- ClC_6H_4	6b	1.3	90	185-187
3	4- FC_6H_4	6c	1.3	87	191-193
4	2- $\text{CH}_3\text{C}_6\text{H}_4$	6d	1.8	88	159-162
5	3- $\text{CH}_3\text{OC}_6\text{H}_4$	6e	1.5	84	204-205
6	4- $\text{CH}_3\text{OC}_6\text{H}_4$	6f	1.7	82	200-202
7	4- $\text{NO}_2\text{C}_6\text{H}_4$	6g	1.25	80	183-184
8	3- $\text{NO}_2\text{C}_6\text{H}_4$	6h	1.5	80	172-174
9	4- $(\text{CH}_3)_2\text{CH-C}_6\text{H}_4$	6i	1.9	81	165-167

^a Yields are related to isolated pure products.

General procedure for the synthesis of xanthene derivatives

A mixture of an aromatic aldehyde (1 mmol), dimedone (1 mmol), 3,4-methylene-dioxyphenol or β -naphthol (1 mmol) and $H_{14}[NaP_5W_{30}O_{110}]$ (0.4 mol%) was stirred at 120 °C for an appropriate time (Tables 1, 2). After completion of the reaction which was monitored by TLC, boiling ethanol was added to the mixture. The catalyst was filtered off and the mixture was cooled to room temperature. The resulting solid product was then removed by filtration and purified by recrystallization from absolute ethanol.

Recycling of the catalyst

After completion of the reaction boiling ethanol was added to the mixture and the catalyst was recycled by a simple filtration, washed with diethyl ether, dried and reused for the next reaction with only a modest loss in activity. The catalyst has been recovered and reused for three times in the synthesis of 7,8-dihydro-7,7-dimethyl-10-phenyl-6H-[1,3]dioxolo[4,5-b]xanthen-9(10H)-one (**5a**) and the results obtained are summarized in Table 3.

Table 3. Reusability of catalyst in the synthesis of **5a**.

Entry	Number of recycle	Time (h)	Yield (%) ^a
1	Fresh	2	88
2	1	2	85
3	2	2	80

^aYields are related to isolated pure products.

Products characterization data

7,7-Dimethyl-10-phenyl-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-b]xanthen-9-one (5a). Anal. calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.77; H, 5.56. M.p. 190-192 °C, IR (KBr) ν/cm^{-1} : 3033, 2963, 1651, 1619, 1502, 1479, 1372, 1333, 1209, 1188, 1144, 1030, 932, 868, 743. ¹H-NMR (500 MHz, $CDCl_3$, δ , ppm): 1.06 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 2.24 (d, J = 16.3 Hz, 1H, CH-6), 2.3 (d, J = 16.3 Hz, 1H, CH-6), 2.56 (s, 2H, CH_2 -8), 4.94 (s, 1H, CH-10), 5.9 (d, J = 1.3 Hz, 1H, CH-2), 5.94 (d, J = 1.3 Hz, 1H, CH-2), 6.53 (s, 1H, ArH), 6.63 (s, 1H, ArH), 7.16-7.18 (m, 1H, ArH), 7.25-7.31 (m, 4H, ArH). ¹³C-NMR (125 MHz, $CDCl_3$, δ , ppm): 27.8, 29.7, 32.6, 38.6, 41.9, 51.2, 98.6, 101.9, 108.7, 113.2, 118.0, 126.8, 128.2, 128.8, 144.3, 145.1, 146.5, 147.2, 165.8, 197.2. MS (m/z): 348 (M^+), 331, 303, 271, 202, 165, 129, 77.

10-(2,4-Dichlorophenyl)-7,7-dimethyl-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-b]xanthen-9-one (5b). Anal. calcd. for $C_{22}H_{18}Cl_2O_4$: C, 63.32; H, 4.35. Found: C, 63.67; H, 4.36. M.p. 214-215 °C, IR (KBr) ν/cm^{-1} : 3082, 3019, 2964, 1651, 1620, 1586, 1561, 1505, 1479, 11441, 1371, 1314, 1124, 1098, 1035, 933, 846, 796, 711, 688, 664. ¹H-NMR (500 MHz, $CDCl_3$, δ , ppm): 1.12 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.23 (d, J = 16.2 Hz, 1H, CH-6), 2.31 (d, J = 16.2 Hz, 1H, CH-6), 2.58 (s, 2H, CH_2 -8), 5.4 (s, 1H, CH-10), 5.9 (d, J = 0.9 Hz, 1H, CH-2), 5.96 (d, J = 0.9 Hz, 1H, CH-2), 6.58 (s, 2H, ArH), 7.12-7.16 (m, 2H, ArH), 7.38 (d, J = 1.7 Hz, 1H, ArH). ¹³C-NMR (125 MHz, $CDCl_3$, δ , ppm): 28.0, 29.7, 32.5, 35.2, 41.9, 51.1, 98.6, 102.0, 108.0, 111.7, 116.4, 127.8, 130.0, 131.5, 133.0, 133.7, 142.5, 144.0, 145.2, 147.5, 165.5, 197.0. MS (m/z): 416 (M^+), 381, 363, 325, 290, 271, 215, 187, 157, 77.

7,7-Dimethyl-10-(2-methylphenyl)-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-b]xanthen-9-one (5c). Anal. calcd. for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.07; H, 6.19. M.p. 176-178 °C, IR (KBr) ν/cm^{-1} : 3059, 3013, 2951, 2890, 1648, 1617, 1509, 1482, 1438, 1372, 1317, 1210, 1186, 1146, 1029, 926, 863, 802, 743, 690, 658. ¹H-NMR (500 MHz, $CDCl_3$, δ , ppm): 1.09 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.23 (d, J = 16.2 Hz, 1H, CH-6), 2.3 (d, J = 16.2 Hz, 1H, CH-6),

2.58 (s, 2H, CH₂-8), 2.74 (s, 3H, CH₃), 5.2 (s, 1H, CH-10), 5.87 (d, J = 1.2 Hz, 1H, CH-2), 5.93 (d, J = 1.2 Hz, 1H, CH-2), 6.44 (s, 1H, ArH), 6.62 (s, 1H, ArH), 7.03-7.09 (m, 3H, ArH), 7.16 (d, J = 6.75 Hz, 1H, ArH). ¹³C-NMR (125 MHz, CDCl₃, δ, ppm): 20.4, 27.9, 29.7, 32.6, 34.3, 41.9, 51.2, 98.6, 101.9, 108.3, 113.7, 118.6, 126.6, 126.7, 129.1, 130.8, 135.3, 144.0, 145.1, 145.5, 147.1, 164.7, 197.3. MS (*m/z*): 362 (M⁺), 345, 271, 215, 187, 157, 138, 77, 44.

7,7-Dimethyl-10-(3-nitrophenyl)-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-b]xanthen-9-one (5d). Anal. calcd. for C₂₂H₁₉NO₆: C, 67.17; H, 4.87; N, 3.56. Found: C, 67.22; H, 4.91; N, 3.49. M.p. 156-158 °C, IR (KBr) ν/cm⁻¹: 3087, 2959, 2922, 1651, 1619, 1528, 1480, 1437, 1373, 1346, 1212, 1143, 1031, 929, 867, 761, 730. ¹H-NMR (500 MHz, CDCl₃, δ, ppm): 1.05 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH-6), 2.32 (d, J = 16.3 Hz, 1H, CH-6), 2.59 (s, 2H, CH₂-8), 5.06 (s, 1H, CH-10), 5.94 (d, J = 1.1 Hz, 1H, CH-2), 5.98 (d, J = 1.1 Hz, 1H, CH-2), 6.46 (s, 1H, ArH), 6.67 (s, 1H, ArH), 7.45 (t, J = 7.7 Hz, 1H, ArH), 7.68 (d, J = 7.7 Hz, 1H, ArH), 8.03-8.05 (m, 2H, ArH). ¹³C-NMR (125 MHz, CDCl₃, δ, ppm): 27.8, 29.6, 32.6, 38.5, 441.9, 51.1, 98.9, 102.1, 108.4, 112.1, 116.1, 122.0, 123.2, 129.6, 134.7, 144.3, 145.5, 147.7, 148.5, 149.0, 165.4, 197.2. MS (*m/z*): 393 (M⁺), 376, 346, 271, 215, 157, 77, 44.

7,7-Dimethyl-10-(4-nitrophenyl)-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-b]xanthen-9-one (5e). Anal. calcd. for C₂₂H₁₉NO₆: C, 67.17; H, 4.87; N, 3.56. Found: C, 67.33; H, 4.83; N, 3.56. M.p. 201-202 °C, IR (KBr) ν/cm⁻¹: 3059, 2965, 2901, 1651, 1619, 1513, 1481, 1441, 1374, 1344, 1208, 1180, 1145, 1033, 931, 873, 848, 828, 748, 704, 629, 601. ¹H-NMR (500 MHz, CDCl₃, δ, ppm): 1.04 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH-6), 2.32 (d, J = 16.3 Hz, 1H, CH-6), 2.58 (s, 2H, CH₂-8), 5.06 (s, 1H, CH-10), 5.94 (d, J = 1.3 Hz, 1H, CH-2), 5.98 (d, J = 1.3 Hz, 1H, CH-2), 6.44 (s, 1H, ArH), 6.66 (s, 1H, ArH), 7.43 (d, J = 8.8 Hz, 2H, ArH), 8.14 (d, J = 8.8 Hz, 2H, ArH). ¹³C-NMR (125 MHz, CDCl₃, δ, ppm): 27.7, 29.7, 32.6, 38.7, 41.9, 51.1, 98.9, 102.1, 108.4, 112.1, 116.0, 124.2, 129.2, 144.3, 145.5, 146.9, 147.8, 153.6, 165.4, 197.0. MS (*m/z*): 393 (M⁺), 376, 346, 271, 215, 187, 157, 139, 77, 44.

7,7-Dimethyl-10-(3-methoxyphenyl)-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-b]xanthen-9-one (5f). Anal. calcd. for C₂₃H₂₂O₅: C, 73.00; H, 5.82. Found: C, 73.17; H, 5.83. M.p. 141-142 °C, IR (KBr) ν/cm⁻¹: 3059, 2963, 1650, 1596, 1481, 1436, 1374, 1317, 1257, 1223, 1194, 1154, 1031, 929, 866, 809, 759, 696. ¹H-NMR (500 MHz, CDCl₃, δ, ppm): 1.08 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 2.26 (d, J = 16.2 Hz, 1H, CH-6), 2.31 (d, J = 16.2 Hz, 1H, CH-6), 2.56 (s, 2H, CH₂-8), 3.8 (s, 3H, OCH₃), 4.92 (s, 1H, CH-10), 5.9 (d, J = 1.3 Hz, 1H, CH-2), 5.95 (d, J = 1.3 Hz, 1H, CH-2), 6.62 (s, 1H, ArH), 6.70-6.72 (dd, J = 8.2 and 2.0, 1H, ArH), 6.80-6.82 (m, 1H, ArH), 6.85 (d, J = 7.6 Hz, 1H, ArH), 7.19 (t, J = 7.9 Hz, 1H, ArH). ¹³C-NMR (125 MHz, CDCl₃, δ, ppm): 27.8, 29.7, 32.5, 38.6, 41.9, 51.2, 55.5, 98.6, 101.9, 108.6, 111.9, 113.0, 114.2, 117.8, 120.6, 129.8, 144.2, 145.1, 147.2, 148.1, 160.1, 164.9, 197.2. MS (*m/z*): 378 (M⁺), 347, 271, 215, 187, 157, 139, 77, 44.

7,7-Dimethyl-10-(4-methoxyphenyl)-6,7,8,10-tetrahydro-9H-[1,3]-dioxolo[4,5-b]xanthen-9-one (5g). Anal. calcd. for C₂₃H₂₂O₅: C, 73.00; H, 5.82. Found: C, 72.93; H, 5.63. M.p. 197-198 °C, IR (KBr) ν/cm⁻¹: 3085, 3034, 2955, 1651, 1615, 1509, 1483, 1441, 1374, 1327, 1299, 1249, 1208, 1171, 1142, 1059, 1026, 921, 855, 785, 757, 659. ¹H-NMR (500 MHz, CDCl₃, δ, ppm): 1.06 (s, 3H, CH₃), 1.15 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH-6), 2.3 (d, J = 16.3 Hz, 1H, CH-6), 2.55 (s, 2H, CH₂-8), 3.78 (s, 3H, OCH₃), 4.9 (s, 1H, CH-10), 5.9 (d, J = 1.3 Hz, 1H, CH-2), 5.95 (d, J = 1.3 Hz, 1H, CH-2), 6.52 (s, 1H, ArH), 6.62 (s, 1H, ArH), 6.80-6.82 (m, 2H, ArH), 7.16-7.18 (m, 2H, ArH). ¹³C-NMR (125 MHz, CDCl₃, δ, ppm): 27.8, 29.7, 32.3, 38.5, 41.2, 51.3, 55.1, 98.2, 101.6, 108.2, 101.2, 113.2, 114.6, 117.7, 129.8, 145.1, 148.2, 149.1, 163.4, 197.1. MS (*m/z*): 378 (M⁺), 347, 294, 271, 215, 187, 96, 77, 44.

12-(4-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (6a). Anal. calcd. for C₂₅H₂₁BrO₂: C, 69.29; H, 4.88. Found: C, 69.30; H, 4.75. M.p. 186-188 °C, IR

(KBr) ν/cm^{-1} : 3062, 2954, 1643, 1592, 1515, 1480, 1374, 1224, 1174, 1070, 1013, 968, 835, 810, 753. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 1.02 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.29 (d, $J = 16.3$ Hz, 1H, CH-8), 2.36 (d, $J = 16.3$ Hz, 1H, CH-8), 2.6 (s, 2H, CH_2 -10), 5.7 (s, 1H, CH-12), 7.25-7.5 (m, 7H, ArH), 7.81-7.84 (m, 2H, ArH), 7.94 (d, $J = 8.4$ Hz, 1H, ArH). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 27.6, 29.7, 32.7, 34.7, 41.8, 51.3, 114.2, 117.4, 117.5, 120.5, 123.9, 125.4, 127.5, 128.9, 129.5, 130.6, 131.6, 131.8, 131.9, 144.2, 148.2, 164.5, 197.2. MS (m/z): 432 (M^+).

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (6b). Anal. calcd. for $\text{C}_{25}\text{H}_{21}\text{ClO}_2$: C, 77.21; H, 5.44. Found: C, 77.72; H, 5.49. M.p. 185-187 °C, IR (KBr) ν/cm^{-1} : 3071, 2951, 2869, 1647.9, 1592, 1513, 1484, 1461, 1431, 1399, 1369, 1230, 1183, 1143, 1088, 1016, 961, 939, 867, 833, 809, 776, 746, 718, 659, 635, 610, 536. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 1.0 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.29 (d, $J = 16.3$ Hz, 1H, CH-8), 2.36 (d, $J = 16.3$ Hz, 1H, CH-8), 2.62 (s, 2H, CH_2 -10), 5.73 (s, 1H, CH-12), 7.18 (d, $J = 8.4$ Hz, 2H, ArH), 7.3 (s, 1H, ArH), 7.32 (d, $J = 8.4$ Hz, 1H, ArH), 7.37 (d, $J = 8.9$ Hz, 1H, ArH), 7.43-7.48 (m, 2H, ArH), 7.81-7.85 (m, 2H, ArH), 7.95 (d, $J = 8.4$ Hz, 1H, ArH). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 27.6, 29.8, 32.7, 34.6, 41.8, 51.3, 114.2, 117.5, 122.0, 123.9, 125.5, 127.6, 128.8, 128.9, 129.5, 130.3, 131.6, 131.9, 132.3, 143.7, 148.1, 164.5, 197.4. MS (m/z): 388 (M^+).

9,9-Dimethyl-12-(4-florophenyl)-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (6c). Anal. calcd. for $\text{C}_{25}\text{H}_{21}\text{FO}_2$: C, 80.62; H, 5.68. Found: C, 80.67; H, 5.66. M.p. 191-193 °C, IR (KBr) ν/cm^{-1} : 3072, 3039, 3003, 2954, 1649, 1595, 1506, 1464, 1372, 1320, 1293, 1226, 1185, 1163, 1143, 1120, 1093, 1069, 1016, 974, 936, 839, 813, 767, 743, 715, 654. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 1 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.3 (d, $J = 16.3$ Hz, 1H, CH-8), 2.36 (d, $J = 16.3$ Hz, 1H, CH-8), 2.62 (s, 2H, CH_2 -10), 5.75 (s, 1H, CH-12), 6.88-6.91 (m, 2H, ArH), 7.3-7.38 (m, 3H, ArH), 7.44 (m, 1H, ArH), 7.47-7.5 (m, 1H, ArH), 7.81-7.84 (m, 2H, ArH), 7.97 (d, $J = 8.4$ Hz, 1H, ArH). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 27.5, 29.7, 32.7, 34.4, 41.8, 51.3, 114.5, 115.4, 115.5, 117.5, 117.8, 123.9, 125.4, 127.5, 128.9, 129.4, 130.3, 130.4, 131.7, 131.9, 140.9, 141.0, 148.2, 160.7, 162.6, 164.3, 197.3. MS (m/z): 372 (M^+).

9,9-Dimethyl-12-(2-methylphenyl)-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (6d). Anal. calcd. for $\text{C}_{26}\text{H}_{24}\text{O}_2$: C, 84.75; H, 6.57. Found: C, 84.69; H, 6.61. M.p. 159-162 °C, IR (KBr) ν/cm^{-1} : 3052, 3016, 2946, 1647, 1594, 1511, 1489, 1463, 1367, 1224, 1174, 1145, 1114, 1066, 1018, 977, 864, 839, 810, 652, 616. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 1.0 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.27 (d, $J = 16.3$ Hz, 1H, CH-8), 2.34 (d, $J = 16.3$ Hz, 1H, CH-8), 2.64 (s, 2H, CH_2 -10), 2.97 (s, 3H, CH_3), 5.8 (s, 1H, CH-12), 6.98-7.00 (m, 2H, ArH), 7.11-7.13 (m, 2H, ArH), 7.35 (d, $J = 8.9$ Hz, 1H, ArH), 7.39-7.42 (m, 1H, ArH), 7.48-7.50 (m, 1H, ArH), 7.77-7.81 (m, 2H, ArH), 7.96 (d, $J = 8.5$ Hz, 1H, ArH). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 20.2, 27.6, 29.7, 32.3, 32.6, 42.0, 51.4, 115.3, 117.6, 119.4, 123.9, 125.2, 126.5, 126.6, 127.3, 128.9, 129.1, 130.2, 131.1, 131.8, 132.0, 135.6, 143.9, 148.1, 164.3, 197.5. MS (m/z): 368 (M^+), 277, 239, 221, 193, 165, 144.

9,9-Dimethyl-12-(3-methoxyphenyl)-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (6e). Anal. calcd. for $\text{C}_{26}\text{H}_{24}\text{O}_3$: C, 81.22; H, 6.29. Found: C, 81.19; H, 6.19. M.p. 204-205 °C, IR (KBr) ν/cm^{-1} : 3058, 3010, 2951, 1646, 1593, 1514, 1481, 1374, 1317, 1273, 1225, 1171, 1143, 1042, 972, 863, 824, 783, 749, 693, 657, 619. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 1.0 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 2.27 (d, $J = 16.3$ Hz, 1H, CH-8), 2.34 (d, $J = 16.3$ Hz, 1H, CH-8), 2.58 (s, 2H, CH_2 -10), 3.7 (s, 3H, OCH_3), 5.7 (s, 1H, CH-12), 6.60-6.64 (dd, $J = 13.5$ and 2.4 Hz, 1H, ArH), 6.91-6.97 (m, 2H, ArH), 7.08-7.13 (m, 1H, ArH), 7.28-7.48 (m, 3H, ArH), 7.76-7.81 (m, 2H, ArH), 8.02 (d, $J = 8.3$ Hz, 1H, ArH). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 27.3, 29.3, 32.3, 34.6, 41.4, 50.9, 55.1, 111.2, 114.0, 114.6, 117.0, 117.6, 121.0, 123.7, 124.9, 126.9,

128.4, 128.8, 129.0, 131.4, 131.5, 146.3, 147.7, 159.4, 163.9, 196.9. MS (m/z): 384 (M^+), 300, 277, 221, 193, 165.

12-(4-methoxyphenyl)-9,10-dihydro-9,9-dimethyl-8H-benzo[a]xanthen-11(12H)-one (6f). Anal. calcd. for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 80.98; H, 6.28. M.p. 200-202 °C, IR (KBr) ν/cm^{-1} : 3059, 3003, 2956, 1665, 1625, 1510, 1460, 1358, 1301, 1259, 1232, 1192, 1162, 1135, 1109, 1028, 997, 931, 841, 721, 682 cm^{-1} ; 1H -NMR (500 MHz, $CDCl_3$, δ , ppm): 0.99 (s, 3H, CH_3), 1.1 (s, 3H, CH_3), 2.24 (d, $J = 16.2$ Hz, 1H, CH), 2.32 (d, $J = 16.3$ Hz, 1H, CH), 2.62 (s, 2H, CH_2), 2.95 (s, 3H, CH_3), 5.7 (s, 1H, CH), 6.95-9.9 (m, 2H, ArH), 7.08-7.1 (m, 2H, ArH), 7.31-7.34 (m, 1H, ArH), 7.4-7.48 (m, 2H, ArH), 7.74-7.79 (m, 2H, ArH), 7.9 (d, $J=8.4$ Hz, 1H, ArH). ^{13}C -NMR (125 MHz, $CDCl_3$, δ , ppm): 27.3, 29.3, 33.2, 34.6, 50.9, 55.3, 111.3, 114.8, 117.6, 124.9, 129.2, 129.9, 131.4, 132.4, 147.7, 152.3, 159.4, 165.8, 196.9. MS (m/z): 384 (M^+), 300, 277, 261, 221, 193, 165.

9,9-Dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (6g). Anal. calcd. for $C_{25}H_{21}NO_4$: C, 75.71; H, 5.30; N, 3.51. Found: C, 75.85; H, 5.33; N, 3.45. M.p. 183-184 °C, IR (KBr) ν/cm^{-1} : 3075, 2951, 1646, 1594, 1515, 1471, 1376, 1342, 1223, 1176, 1144, 1109, 1023, 981, 828, 749, 695, 660, 613. 1H -NMR (500 MHz, $CDCl_3$, δ , ppm): 0.96 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.26 (d, $J = 16.4$ Hz, 1H, CH-8), 2.36 (d, $J = 16.4$ Hz, 1H, CH-8), 2.62 (s, 2H, CH_2 -10), 5.8 (s, 1H, CH-12), 7.36 (d, $J = 8.9$ Hz, 1H, ArH), 7.42-7.49 (m, 2H, ArH), 7.52-7.55 (m, 2H, ArH), 7.81-7.86 (m, 3H, ArH), 8.04-8.07 (m, 2H, ArH). ^{13}C -NMR (125 MHz, $CDCl_3$, δ , ppm): 27.5, 29.7, 32.7, 35.3, 39.2, 51.2, 113.4, 116.5, 117.5, 123.5, 124.0, 125.7, 127.8, 129.0, 129.8, 130.0, 131.5, 132.0, 146.8, 148.2, 152.3, 165.0, 197.0. MS (m/z): 399 (M^+), 382, 277, 239, 221, 193, 165.

12-(3-Nitrophenyl)-9,10-dihydro-9,9-dimethyl-8H-benzo[a]xanthen-11(12H)-one (6h). Anal. calcd. for $C_{25}H_{21}NO_4$: C, 75.71; H, 5.30; N, 3.51. Found: C, 75.45; H, 5.22; N, 3.65. M.p. 172-174 °C, IR (KBr) ν/cm^{-1} : 3068, 2955, 2869, 1648, 1594, 1528, 1467, 1373, 1347, 1223, 1170, 1083, 1022, 9741, 810. 1H -NMR (500 MHz, $CDCl_3$, δ , ppm): 0.97 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.26 (d, $J = 16.3$ Hz, 1H, CH-8), 2.35 (d, $J = 16.3$ Hz, 1H, CH-8'), 2.63 (s, 2H, CH_2 -10), 5.83 (s, 1H, CH-12), 7.36-7.50 (m, 4H, ArH), 7.81-7.86 (m, 4H, ArH), 7.93-7.97 (m, 1H, ArH), 8.12-8.14 (m, 1H, ArH). ^{13}C -NMR (125 MHz, $CDCl_3$, δ , ppm): 27.5, 29.7, 34.7, 39.3, 39.2, 51.1, 113.3, 116.5, 117.5, 123.5, 124.0, 125.7, 127.8, 129.0, 129.8, 130.0, 131.5, 132.0, 133.1, 136.5, 149.7, 150.1, 148.2, 152.5, 165.0, 197.1. MS (m/z): 399 (M^+), 382, 277, 239, 221, 193, 165.

9,9-Dimethyl-12-(4-isopropylphenyl)-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (6i). Anal. calcd. for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12. Found: C, 84.81, H, 6.12. M.p. 165-167 °C, IR (KBr) ν/cm^{-1} : 3079, 3047, 2958, 1649, 1595, 1511, 1464, 1419, 1371, 1291, 1231, 1186, 1145, 1118, 1056, 1020, 976, 939, 892, 818, 779, 747, 660, 616. 1H -NMR (500 MHz, $CDCl_3$, δ , ppm): 1.0 (s, 3H, CH_3), 1.16 (d, $J = 7.1$ Hz, 6H, $2CH_3$), 1.18 (s, 3H, CH_3), 2.3 (d, $J = 16.2$ Hz, 1H, CH-8), 2.35 (d, $J = 16.2$ Hz, 1H, CH-8), 2.6 (d, $J = 17.4$ Hz, 1H, CH-10), 2.64 (d, $J = 17.4$ Hz, 1H, CH-10), 2.77-2.83 (sep., $J = 7.1$ Hz, 1H, CH), 5.7 (s, 1H, CH-12), 7.05 (d, $J = 8.2$ Hz, 2H, ArH), 7.28(d, $J = 8.2$ Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.36-7.43 (m, 2H, ArH), 7.47-7.5 (m, 1H, ArH), 7.79-7.81 (m, 2H, ArH), 8.0 (d, $J = 8.4$ Hz, 1H, ArH) ppm. ^{13}C -NMR (125 MHz, $CDCl_3$, δ , ppm): 24.2, 24.3, 27.8, 29.6, 32.7, 33.9, 34.7, 41.8, 51.4, 114.9, 117.5, 118.4, 124.2, 125.2, 126.7, 127.3, 128.6, 128.8, 129.1, 131.9, 142.5, 146.9, 148.2, 164.3, 197.4. MS (m/z): 396 (M^+).

RESULTS AND DISCUSSION

To optimize the catalytic system, the synthesis of 7,8-dihydro-10-phenyl-7,7-dimethyl-6H-[1,3]dioxolo[4,5-b]xanthen-9(10H)-one (**5a**) from the condensation of 3,4-methylene-dioxyphenol, benzaldehyde and dimedone under solvent free conditions (Table 4) was used as a

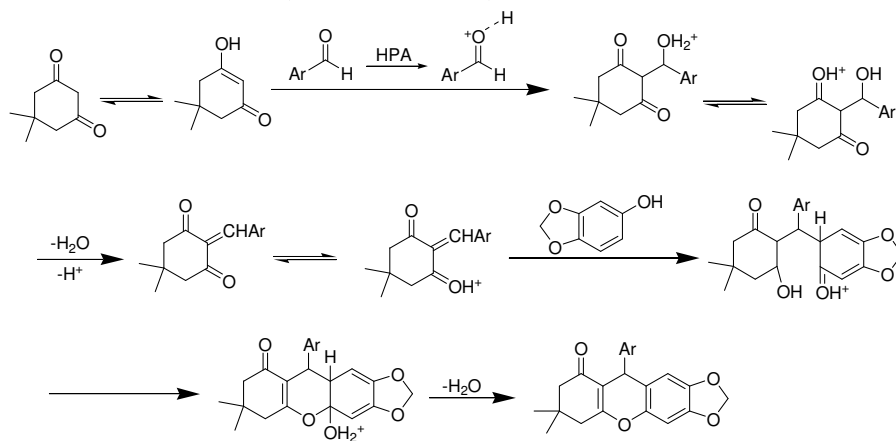
model reaction. Firstly, we study the relation between the rate of the model reaction and temperature and the best results were obtained at 120 °C (Table 4). The best catalytic activity of $H_{14}NaP_5W_{30}O_{110}$ was optimized to be 0.4 mol% and any excess of the catalyst, beyond this proportion, did not show further increase in the conversion and yield (Table 4).

Table 4. Optimization of the reaction conditions in the synthesis of **5a** and **6c** under solvent-free conditions.

Entry	Catalyst amount (g)	Temperature (°C)	Time (h)	Yield (%) ^a
1	-	120	24	NR
2	0.010	120	25	30
3	0.050	120	2	88
4	0.10	120	3	88
5	0.050	24	12	NR
6	0.050	50	12	10
7	0.050	80	2	65
8 ^b	-	120	24	NR
9 ^b	0.010	120	20	40
10 ^b	0.050	120	1.6	87
11 ^b	0.10	120	1.6	87

^aYields are related to isolated pure products. ^bsynthesis of 12-(4-fluorophenyl)-9,10-dihydro-9,9-dimethyl-8*H*-benzo[*a*]xanthen-11(12*H*)-one.

We also examined the effect of the catalyst amount in the synthesis of 12-(4-fluorophenyl)-9,10-dihydro-9,9-dimethyl-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**6c**) under solvent-free conditions and obtained the same results (Table 4, entries 8-11).



Scheme 2

The optimized conditions were used for the synthesis of 7,8-dihydro-10-aryl-7,7-dimethyl-6*H*-[1,3]dioxolo[4,5-*b*] xanthen-9(10*H*)-one and 12-aryl-9,10-dihydro-9,9-dimethyl-8*H*-benzo[*a*]xanthen-11(12*H*)-one derivatives. It was found that this method is effective with a variety of substituted aromatic aldehydes independently of the nature of the substituents on the aromatic ring (Tables 1 and 2). It is noteworthy to mention that the catalyst is recyclable and could be reused without significant loss of activity. After completion of the model reaction, boiling ethanol was added to the mixture and the catalyst was filtered off by a simple filtration, washed with diethyl ether, dried and reused for the next reaction with only a modest loss in

activity (Table 3). A possible mechanism for the synthesis of 7,8-dihydro-10-aryl-7,7-dimethyl-6H-[1,3]dioxolo[4,5-b] xanthen-9(10H)-one derivatives is given in Scheme 2.

In summary, we have reported a high yielding, simple, convenient, straightforward and practical one-pot procedure for the synthesis of some novel 7,8-dihydro-10-aryl-7,7-dimethyl-6H-[1,3]dioxolo[4,5-b] xanthen-9(10H)-ones (**5**) and 12-aryl-9,10-dihydro-9,9-dimethyl-8H-benzo[*a*]xanthen-11(12H)-one derivatives (**6**) from the condensation of 3,4-methylene-dioxyphenol or β -naphthol with aldehydes and dimedone under solvent-free condition. The conditions are mild and a wide range of functional groups can be tolerated. Using heteropolyacid as catalyst offers advantages including simplicity of operation, easy work-up, recycling of the catalyst and high yields of products.

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