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Amberlyst-15 Catalyzed Synthesis of 12-Aryl-12*H*-benzo[i][1,3]-dioxolo[4,5-b]xanthene-6,11-diones and 14-Aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones under Solvent-Free Condition

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Three-component one-pot synthesis of some novel 12-aryl-12*H*-[1,3]-dioxolo[4,5-b]benzo[i]xanthene-6,11-diones and 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones, from condensation of 3,4-methylenedioxyphenol or β-naphthol, aldehydes and 2-hydroxy-1,4-naphthoquinone in the presence of Amberlyst-15 under solvent-free conditions at 120 ºC is reported.

Key Words: Benzo[i][1,3]dioxolo[4,5-b]xanthene, Dibenzo[a,i]xanthene, Amberlyst-15, Solvent-free.

INTRODUCTION

Xanthenes and benzoxanthenes are important biologically active heterocyclic compounds, which posses such as antibacterial[1], antiviral[2] and antiinflammatory activities[3], as well as photodynamic therapy[4] and for antagonism of the paralyzing action of zoxazolamine[5]. The other useful applications of these heterocycles are as dyes[6], fluorescent materials for visualization of biomolecules[7] and in laser technologies[8]. Many procedures have been developed for the synthesis of xanthenes and benzoxanthenes, which include trapping of benzynes by phenols[9], cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone[10], cyclodehydrations[11] and intramolecular phenyl carbonyl reaction of aldehydes with β-naphthol[12], furthermore, the synthesis of benzoxanthenes and their related products include the reaction of β-naphthol with formamide[13], carbon monoxide[14], 2-naphthol-1-methanol[15], aldehydes and cyclic 1,3-dicarbonyl compounds[16]. 1,3-Dioxolo-[4,5-b]benzopyrans are "privileged medicinal scaffolds", which are widely found in natural products and have potent antiinflammatory activity[17].

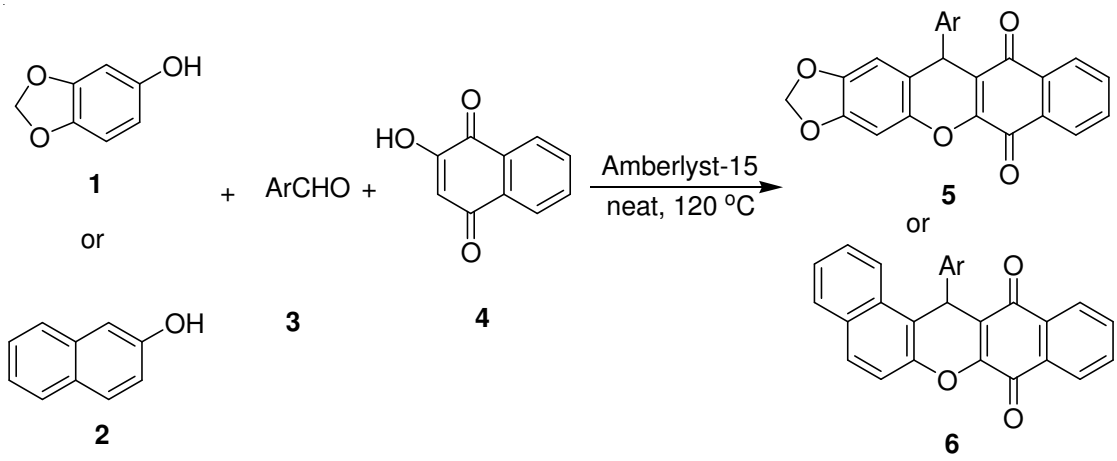
In recent years, the use of solid acidic catalysts has offered important advantages in organic synthesis, for example, operational simplicity, environmental compatibility, non-toxic, reusability, low cost and ease of isolation. A tremendous upsurge of interest in various chemical transformations processes by catalysts under heterogeneous conditions has occurred. One of those heterogeneous catalysts is Amberlyst-15. It makes reaction processes convenient, more economic and environmentally benign. Owing to the numerous advantages associated with this cheap and non-hazardous catalyst, Amberlyst-15 has been explored as a powerful catalyst for various organic transformations under mild conditions[18].

In this paper, we report an Amberlyst-15 catalyzed simple, efficient and environmentally benign synthesis of 12-aryl-12*H*-benzo[i][1,3]-dioxolo[4,5-b]xanthene-6,11-diones in excellent yields by condensing a variety of aldehydes with 3,4-methylenedioxyphenol and 2-hydroxy-1,4-naphthoquinone under solvent-free conditions. During our study, we also observed the formation of 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones in excellent yields by one-pot condensation of β-naphthol with aromatic aldehydes and 2-hydroxy-1,4- naphthoquinone in the presence of Amberlyst-15 (**Scheme-I**).

EXPERIMENTAL

NMR spectra were determined on Bruker AV-400 spectrometer at room temperature using TMS as internal standard, coupling constants (*J*) were measured in Hz; elemental analysis were performed by a Vario-III elemental analyzer; melting points were determined on a XT-4 binocular microscope and were uncorrected; commercially available reagents were used throughout without further purification unless otherwise stated.

General procedure for the preparation of 5 and 6: A mixture of 3,4-methylenedioxyphenol or β-naphthol (1 mmol), aldehyde (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol) and Amberlyst-15 (30 mg) was heated at 120 ºC for an appropriate time and monitored by TLC until the final conversion. After cooling, the reaction mixture was washed with $CHCl_3$ and filtered to recover the catalyst. The solvent was evaporated and the crude product puried by silica gel column chromatography using $CHCl_3$ as eluent to afford the pure product.



Scheme-I

12-Phenyl -12*H*-benzo[i][1,3]-dioxolo[4,5-b] xanthene-6,11-dione (5a): Marron powder, m.p. 242-243 ºC; IR (KBr, ν_{max}, cm^{-1}): 1706, 1642, 1607, 1577, 1504, 1481, 1374, 1290, 1188, 1141, 1031, 913; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.15 (d, 1H, *J* = 7.6 Hz), 8.12 (d, 1H, *J* = 7.6 Hz), 8.04-7.70 (m, 2H), 8.44-7.13 (m, 6H), 6.61 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.12, 178.10, 158.09, 147.39, 145.56, 142.89, 135.63, 135.12, 132.91, 131.98, 131.38, 130.66, 130.46, 130.17, 130.02, 129.56, 128.24, 127.24, 124.62, 115.70, 107.77, 101.82, 98.42, 35.61. Anal. calcd. (%) for $C_{24}H_{14}O_5$: C 75.39, H 3.69; found (%): C 75.52, H 3.51.

12-(4-Chlorophenyl)-12*H*-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6,11-dione (5b): Marron powder, m.p. 229-230 ºC; IR (KBr, ν_{max}, cm^{-1}): 2903, 1701, 1646, 1606. 1502, 1481, 1371, 1288, 1242, 1183, 1143, 1035, 935, 909, 776; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.14 (d, 1H, *J* = 7.6 Hz), 7.99 (d, 1H, *J* = 7.6 Hz), 7.90-7.68 (m, 2H), 7.35-7.13 (m, 5H), 6.82 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.21, 178.14, 157.59, 147.51, 145.77, 143.37, 142.88, 135.15, 132.73, 131.38, 130.65, 129.99, 129.57, 129.42, 128.72, 126.71, 124.59, 115.93, 114.85, 110.18, 108.06, 101.92, 98.54, 37.80; Anal. calcd. (%) for $C_{24}H_{13}O_5Cl$: C 69.16, H 3.14; found (%): C 69.32, H 3.01.

12-(4-Methoxylphenyl)-12*H*-benzo[i][1,3]-dioxolo[4,5-b]xanthene-6,11-dione (5c): Marron powder, m.p. 201-202 ºC; IR (KBr, ν_{max}, cm^{-1}): 2982, 1736, 1700, 1645, 1606, 1511, 1479, 1372, 1287, 1255, 1139, 1037, 910, 834; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.13 (d, 1H, *J* = 8.0 Hz), 7.98 (d, 1H, *J* = 7.6 Hz), 7.89-7.67 (m, 2H), 7.21-7.12 (m, 3H), 6.80-6.78 (m, 3H), 6.04 (s, 1H), 5.99 (s, 1H), 5.03 (s, 1H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.35, 178.31, 158.39, 157.29, 147.24, 145.63, 143.42, 136.79, 135.07, 131.16, 130.90, 129.98, 129.33, 129.18, 124.49, 116.83, 115.58, 113.91, 108.18, 101.80, 98.41, 55.22, 37.48. Anal. calcd. (%) for $C_{25}H_{16}O_6$: C 72.81, H 3.91; found (%): C 72.92, H 3.82.

12-(4-Methylphenyl)-12*H*-benzo[i][1,3]-dioxolo[4,5-b] xanthene-6,11-dione (5d): Orange powder, m.p. 2215-216 ºC; IR (KBr, ν_{max}, cm^{-1}): 2932, 1700, 1644, 1575, 1480, 1373, 1288, 1234, 1186, 1142, 1037, 912, 769; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.14 (d, 1H, *J* = 7.6 Hz), 7.98 (d, 1H, *J* = 7.6 Hz), 7.91-7.88 (m, 1H), 7.71-7.68 (m, 1H), 7.19-7.03 (m, 5H), 6.81 (s, 1H), 6.04 (s, 1H), 5.98 (s, 1H), 5.05 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 178.24, 178.05, 157.51, 147.24, 145.42, 143.16, 142.66, 136.10, 135.46, 131.78, 130.71, 130.66, 129.44, 128.84, 127.90, 124.77, 117.32, 114.78, 108.22, 102.23, 98.99, 37.65, 20.95. Anal. calcd. (%) for $C_{25}H_{16}O_5$: C 75.75, H 4.07; found (%): C 75.84, H 4.01.

12-(4-Nitrophenyl)-12*H*-benzo[i][1,3]-dioxolo[4,5-b] xanthene-6,11-dione (5e): Marron powder, m.p. 219-220 ºC; IR (KBr, ν_{max}, cm^{-1}): 2991, 1694, 1645, 1604, 1576, 1518, 1481, 1375, 1349, 1290, 1235, 1187, 1144, 1036, 914, 834; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.17 (d, 1H, *J* = 8.0 Hz), 8.12-8.10 (m, 2H), 8.00 (d, 1H, *J* = 7.6 Hz), 7.92-7.88 (m, 1H), 7.74-7.70 (m, 1H), 7.64-7.62 (m, 2H), 7.18 (s, 1H), 6.86 (s, 1H), 6.06 (s, 1H), 6.00 (s, 1H), 5.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.08, 177.92, 158.07, 151.29, 147.92, 146.72, 146.01, 143.33, 135.29, 131.71, 130.33, 130.00, 129.55, 129.31, 129.20, 124.75, 123.94, 123.63, 114.75, 113.87, 107.91, 102.09, 98.78, 38.35; Anal. calcd. (%) for $C_{27}H_{13}NO_7$: C 67.45, H 3.07, N 3.28; found (%): C 67.32, H 3.14, N 3.20.

12-(3-Nitrophenyl)-12*H*-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6,11-dione (5f): Orange powder, m.p. 232-233 ºC; IR (KBr, ν_{max}, cm^{-1}): 2894, 1700, 1644, 1604, 1575, 1528, 1482, 1374, 1350, 1289, 1233, 1188, 1144, 1039, 937, 774, 731; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.19-8.15 (m, 2H), 8.15-7.98 (m, 2H), 7.90-7.531 (m, 4H), 7.16 (s, 1H), 6.86 (s, 1H), 6.05 (s, 1H), 6.00 (s, 1H), 5.32 (s, 1H); $_{13}$C NMR ($CDCl_3$, 100 MHz) δ: 178.01, 177.99, 157.97, 148.48, 147.89, 146.30, 146.01, 143.36, 135.29, 134.77, 131.67, 130.38, 130.05, 129.53, 129.44, 124.86, 123.13, 122.16, 114.81, 113.93, 107.94, 102.07, 98.84, 38.27. Anal. calcd. (%) for $C_{27}H_{13}NO_7$: C 67.45, H 3.07, N 3.28; found (%): C 67.52, H 3.10, N 3.25.

12-(3,4-Dichlorophenyl)-12*H*-benzo[i][1,3]-dioxolo-[4,5-b]xanthene-6,11-dione (5g): Orange powder, m.p. 227-228 ºC; IR (KBr, ν_{max}, cm^{-1}): 2975, 1694, 1644, 1608, 1503, 1480, 1374, 1291, 1238, 1144, 1037, 915, 863; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.13 (d, 1H, *J* = 7.6 Hz), 8.09 (d, 1H, *J* = 7.6 Hz), 7.81-7.78 (m, 1H), 7.64-7.60 (m, 1H), 7.34-7.18 (m, 3H), 6.85 (s, 1H), 6.51 (s, 1H), 6.02 (s, 1H), 5.99 (s, 1H), 5.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.14, 178.03, 157.76, 147.75, 145.92, 144.46, 143.35, 135.19, 132.63,

131.54, 131.08, 130.50, 130.45, 130.11, 130.04, 129.48, 127.78, 124.69, 115.19, 114.25, 107.97, 102.01, 98.66, 37.71; Anal. calcd. (%) for $C_{24}H_{12}O_5Cl_2$: C 63.88, H 2.68; found (%): C 64.02, H 2.52.

12-(4-Fluorophenyl)-12*H*-benzo[i][1,3]-dioxolo[4,5-b] xanthene-6,11-dione (5h): Marron powder, m.p. 251-252 ºC; IR (KBr, ν_{max}, cm^{-1}): 2930, 1701, 1646, 1605, 1502, 1480, 1373, 1288, 1186, 1143, 1035, 935, 909; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.14 (d, 1H, *J* = 7.6 Hz), 7.99 (d, 1H, *J* = 7.6 Hz), 7.90-7.86 (m, 1H), 7.71-7.67 (m, 1H), 7.36-7.03 (m, 5H), 6.82 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.12 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 178.22, 177.97, 157.61, 147.39, 145.51, 143.19, 141.71, 135.40, 131.82, 130.77, 130.65, 130.03, 129.95, 128.80, 124.80, 116.91, 115.65, 115.43, 114.46, 108.19, 102.29, 99.06, 37.29; Anal. calcd. (%) for $C_{24}H_{13}O_5F$: C 72.00, H 3.27; found (%): C 72.15, H 3.18.

14-Phenyl-14*H*-dibenzo[a,i]xanthene-8,13-dione (6a): Yellow powder, m.p. 319-320 ºC; IR (KBr, ν_{max}, cm^{-1}): 3082, 1663, 1635, 1590, 1575, 1370, 1286, 1237, 1213; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.17 (d, 1H, *J* = 7.6 Hz), 8.12 (d, 1H, *J* = 7.6 Hz), 7.99 (d, 1H, *J* = 8.4 Hz), 7.91-7.77 (m, 3H), 7.61-7.41 (m, 6H), 7.20 (t, 2H, *J* = 8.0 Hz), 7.12-7.09 (m, 1H), 5.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.33, 178.29, 157.19, 147.30, 143.12, 135.11, 131.89, 131.22, 131.01, 130.89, 130.03, 129.51, 129.39, 128.58, 128.55, 127.45, 126.84, 125.53, 124.53, 123.78, 116.88, 116.77, 116.57, 35.16; Anal. calcd. (%) for $C_{27}H_{16}O_3$: C 83.49, H 4.15; found (%): C 83.25, H 4.12.

14-(4-Chlorophenyl)-14*H*-dibenzo[a,i]xanthene-8,13-dione (6b): Yellow powder, m.p. 305-306 ºC; IR (KBr, ν_{max}, cm^{-1}): 3046, 1667, 1637, 1591, 1577, 1488, 1367, 1286, 1235, 1213; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.16 (d, 1H, *J* = 7.6 Hz), 8.13 (d, 1H, *J* = 7.6 Hz), 7.92-7.77 (m, 4H), 7.62-7.44 (m, 4H), 7.34 (d, 2H, *J* = 8.4 Hz), 7.15 (d, 2H, *J* = 8.4 Hz), 5.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.24, 178.18, 157.30, 147.23, 141.59, 135.17, 132.65, 131.90, 131.39, 130.81, 130.68, 130.00, 129.96, 129.79, 129.47, 128.70, 128.65, 127.58, 125.67, 124.60, 123.57, 116.79, 116.26, 116.00, 34.62; Anal. calcd. (%) for $C_{27}H_{15}O_3Cl$: C 76.69, H 3.58; found (%): C 76.48, H 3.62.

14-(4-Methylphenyl)-14*H*-dibenzo[a,i]xanthene-8,13-dione (6c): Yellow powder, m.p. 255-256 ºC; IR (KBr, ν_{max}, cm^{-1}): 2920, 1665, 1637, 1591, 1577, 1364, 1286, 1237, 1213; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.16 (d, 1H, *J* = 8.0 Hz), 8.11 (d, 1H, *J* = 7.6 Hz), 7.99 (d, 1H, *J* = 8.0 Hz), 7.89-7.76 (m, 3H), 7.60-7.42 (m, 4H), 7.29 (d, 2H, *J* = 8.0 Hz), 7.00 (d, 2H, *J* = 7.6 Hz), 5.90 (s, 1H), 2.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.34, 178.20, 157.08, 147.24, 140.27, 136.48, 135.08, 131.87, 131.16, 131.01, 130.92, 129.99, 129.41, 129.34, 129.24, 128.52, 128.42, 127.43, 125.50, 124.49, 123.78, 117.02, 116.78, 116.70, 34.70, 20.95; Anal. calcd. (%) for $C_{28}H_{18}O_3$: C 83.57, H 4.51; found (%): C 83.49, H 4.63.

14-(4-Nitrophenyl)-14*H*-dibenzo[a,i]xanthene-8,13-dione (6d): Yellow powder, m.p. 332-333 ºC; IR (KBr, ν_{max}, cm^{-1}): 3076, 1664, 1636, 1590, 1576, 1519, 1349, 1285, 1236, 1213; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.20 (d, 1H, *J* = 7.6 Hz), 8.15 (d, 1H, *J* = 7.6 Hz), 8.06 (d, 2H, *J* = 8.8 Hz), 7.97-7.81 (m, 4H), 7.66-7.49 (m, 6H), 6.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.15, 177.98, 157.84, 150.06, 147.29, 146.68, 135.30, 131.99, 131.73, 130.65, 130.40, 130.32, 130.06, 129.63, 129.57, 128.83, 127.87, 125.91, 124.77, 123.88, 123.26, 116.83, 115.35, 115.03, 35.25; Anal. calcd. (%) for $C_{27}H_{15}NO_5$: C 74.82, H 3.49, N 3.23; found. (%): C74.91, H 3.38, N 3.29.

14-(3-Nitrophenyl)-14*H*-dibenzo[a,i]xanthene-8,13-dione (6e): Yellow powder, m.p. 304-305 ºC; IR (KBr, ν_{max}, cm^{-1}): 3072, 1652, 1635, 1588, 1576, 1528, 1345, 1289, 1239, 1216; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.22 (d, 1H, *J* = 8.0 Hz), 8.15 (d, 1H, *J* = 8.0 Hz), 8.12 (s, 1H), 8.00-7.82 (m, 6H), 7.66-7.61 (m, 2H), 7.52-7.41 (m, 3H), 6.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.14, 178.02, 157.73, 148.56, 147.33, 145.09, 135.31, 135.08, 132.03, 131.68, 130.60, 130.42, 130.35, 130.09, 129.59, 129.38, 128.87, 127.82, 125.85, 124.88, 123.32, 123.26, 122.14, 116.97, 115.27, 115.19, 35.20; Anal. calcd. (%) for $C_{27}H_{15}NO_5$: C 74.82, H 3.49, N 3.23; found (%): C74.76, H 3.56, N 3.25.

RESULTS AND DISCUSSION

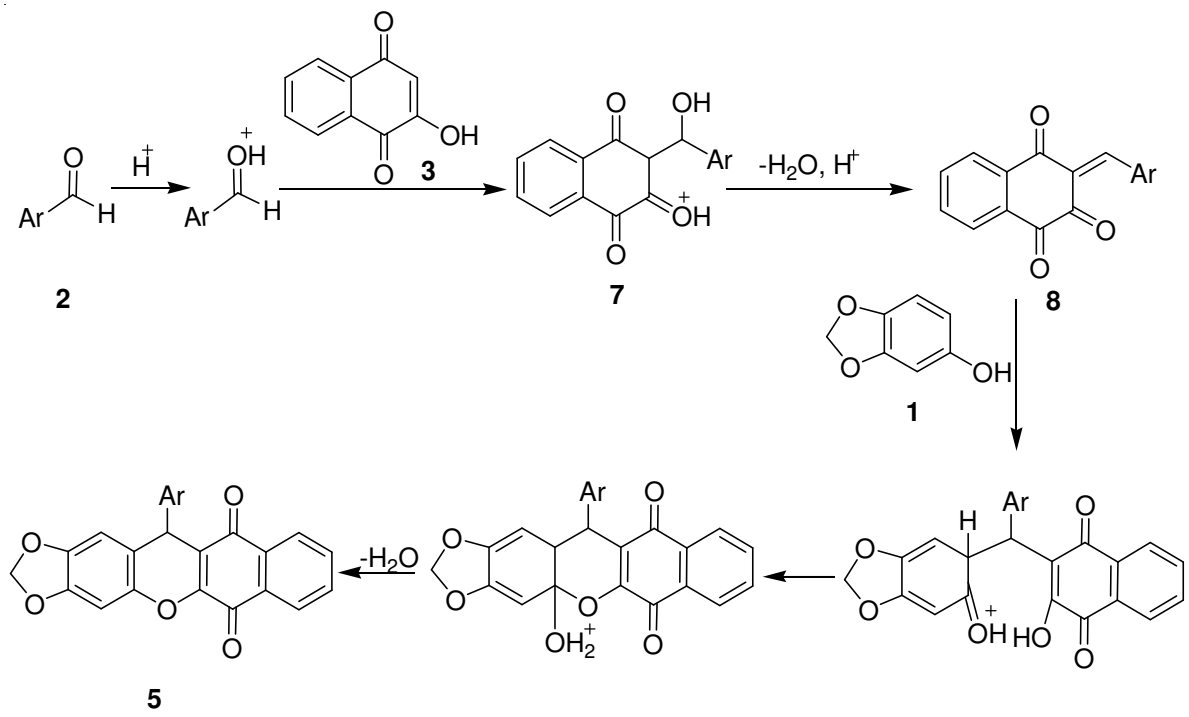
Initially, to optimize the amount of catalyst and the reaction temperature, the reaction of 3,4-methylenedioxyphenol with benzaldehyde and 2-hydroxy-1,4- naphthoquinone was studied under solvent-free conditions in the presence of Amberlyst-15 at different temperatures. The results were summarized in Table-1 and showed that the reaction using 30 mg/mmol Amberlyst-15 at 120 ºC proceeded in highest yield.

TABLE-1
AMOUNTS OF CATALYST AND TEMPERATURE OPTIMIZATION FOR THE SYNTHESIS OF 12-PHENYL-12*H*-BENZO[i][1,3]-DIOXOLO[4,5-b]XANTHENE-6,11-DIONE[a]

Entry	Amberlyst-15 (mg/mmol)	Temp. (ºC)	Time (h)	Yield (%)[b]
1	30	25	5	0
2	30	50	3	0
3	30	90	2	56
4	30	100	2	69
5	30	110	2	75
6	0	120	5	<10
7	10	120	2	63
8	20	120	1.5	78
9	30	120	1.5	87
10	40	120	1.5	87
11	50	120	1.5	86
12	20	130	1.5	79
13	30	130	1	83
14	30	140	1	86

[a]Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); benzaldehyde (1 mmol); 2-hydroxy-1,4-naphthoquinone (1 mmol); neat. [b]Isolated yield.

Based on the optimized reaction conditions, several syntheses of 12-aryl-12*H*-benzo[i][1,3]-dioxolo[4,5-b]xanthene-6,11-diones from the condensation of 3,4-methylenedioxyphenol, 2-hydroxy-1,4-naphthoquinone and a wide range of aromatic aldehydes utilizing Amberlyst-15 under solvent-free conditions at 120 ºC were examined. All reactions were complete within 1-2 h, as indicated in Table-2, in all cases the reactions afforded the desired products in excellent yields. When this reaction was carried out with aliphatic aldehyde such as butanal or pentanal, TLC and ^{1}H NMR spectra of the reaction mixture showed a combination of starting materials and numerous



Scheme-II

TABLE-2
PREPARATION OF 12-ARYL-12*H*-BENZO[i][1,3]-DIOXOLO[4,5-b]XANTHENE-6,11-DIONES CATALYZED BY AMBERLYST-15[a]

Entry	Ar	Time (h)	Product	Yield (%)[b]
1	C_6H_5	1.5	**5a**	87 (86, 83, 84)[c]
2	4-Cl-C_6H_4	1.5	**5b**	85
3	4-MeO-C_6H_4	1.0	**5c**	82
4	4-Me-C_6H_4	1.0	**5d**	92
5	4-NO_2-C_6H_4	2.0	**5e**	80
6	3-NO_2-C_6H_4	2.0	**5f**	86
7	3,4-Cl_2-C_6H_3	1.5	**5g**	85
8	2-F-C_6H_4	1.0	**5h**	82

[a]Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); aldehyde (1 mmol); 2-hydroxy-1,4-naphthoquinone (1 mmol); Amberlyst-15 (30 mg); 120 °C; neat. [b]Isolated yield. [c]Yields after three times of catalyst recovery.

products, the yield of the expected product was very poor. All of the products **5** exhibited a singlet in their ^{1}H spectra at δ = 5.03-5.52 ppm for H-12, two singlet in their ^{1}H spectra at δ = 5.98-6.05 ppm for H-1, 4, a distinguishing peak at δ = 35.61-38.35 ppm for C-12 in their ^{13}C NMR spectra and a distinguishing peak at δ = 98.42- 99.06 ppm for C-2' in their ^{13}C NMR spectra. There were two overlapping doublets at δ = 7.98-8.15 ppm, which probably arise form the protons peri to the quinone C=O. The resonances of two non-equivalent carbonyl groups in their ^{13}C NMR spectrum of **5** appeared at δ = 177.92-178.35 ppm. In these experiments the catalyst was isolated by filtration and could be recycled up to three times without significant loss of activity (entry 1).

The reaction likely proceeds *via* initial formation of oxonium species **7**, which then undergo dehydration to give olefin **8**. Subsequent Michael-type addition of 3,4-methylenedioxyphenol **1** to the olefin fllowed by cyclization and dehydration to afford the corresponding products **5a-5h**.

Encouraged by these results, it is observed that the present protocol could safely be extended to the condensation reaction of β-naphthol with aromatic aldehydes and 2-hydroxy-1,4-naphthoquinone in same conditions. 14-Aryl-14*H*-dibenzo-[a,i]xanthene-8,13-diones were obtained in excellent yields (Table-3). But we extended present protocol by using substituted phenols (*e.g.*, 4-methoxyphenol, 4-chlorophenol, 3-nitrophenol and 1-naphthol) instead of 2-naphthol. The reactions were very sluggish and no product formation was observed.

TABLE-3
PREPARATION OF 14-ARYL-14*H*-DIBENZO[a,i]XANTHENE-8,13-DIONES CATALYZED BY AMBERLYST-15[a]

Entry	Ar	Time (h)	Product	Yield (%)[b]
1	C_6H_5	1	6a	90
2	4-Cl-C_6H_4	1	6b	89
4	4-Me-C_6H_4	1	6c	88
5	4-NO_2-C_6H_4	1.5	6d	89
6	3-NO_2-C_6H_4	2	6e	86

[a]Reaction conditions: β-naphthol (1 mmol); aldehyde (1 mmol); 2-hydroxynaphthalene-1,4-dione (1 mmol); Amberlyst-15 (30 mg); 120 °C; neat. [b]Isolated yield.

Conclusion

We have developed a simple and highly efficient practical method for synthesis of some novel 12-aryl-12*H*-benzo[i][1,3]-dioxolo[4,5-b] xanthene-6,11-diones and 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones using Amberlyst-15 under solvent-free conditions. The notable features of this procedure are simple experimental procdure and excellent yields (82-92 %), which make it a useful and attractive process for the synthesis of 12-aryl-12*H*-benzo[i][1,3]-dioxolo[4,5-b]xanthene-6,11-diones and 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones.

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