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Microwave-assisted one-pot synthesis of 1-amidoalkyl 2-naphthols and dibenzo [*a,j*] xanthenes using phosphorus pentoxide on solid supports

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ABSTRACT

A convenient, efficient and practical procedure for the synthesis of 1-amidoalkyl 2-naphthols is described by condensation of aromatic aldehydes with amides and 2-naphthol in the presence of P_2O_5/SiO_2 as an efficient catalyst. Moreover, in the present of this catalyst, the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes is studied by condensation of aldehydes with 2-naphthol. Using solvent-free conditions, non-toxic and inexpensive materials, simple and clean work-up, short reaction times and high yields of the products are the advantages of this method.

***Keywords**: 1-Amidoalkyl 2-naphthols, Dibenzoxanthenes, Phosphorus pentoxide, Solid supports, Microwave irradiation.*

1. Introduction

Phosphorus pentoxide has been frequently used in various types of organic reactions as a dehydration reagent, but it is difficult to handle due to its moisture sensitivity at room temperature. This problem is not solved by replacement of P_2O_5 with polyphosphoric acid (PPA) because this compound is extremely viscous and is almost impossible to stir effectively or use conveniently at temperatures below 60-90 °C. Moreover, it is difficult to handle on a large scale, even at elevated temperatures. Furthermore, some organic compounds are only sparsely soluble in PPA. Finally, hydrolysis of PPA in work-up procedures is always tedious and time-consuming. Eaton and his co-workers [1] have reported a solution of phosphorus pentoxide in methanesulfonic acid (P_2O_5/MSA) as a convenient strong acid and dehydrating reagent which can be used instead of PPA in many reactions [2-4]. General solubility of organic compounds in this mixture, its low viscosity, and the simplicity of work-up are the advantages of this reagent. However, using excess amount of methanesulfonic acid and sulfonylation of aromatic compounds, as a side reaction, which can occur with MSA in the presence of P_2O_5, are disadvantages of this reagent. Recently, the use of P_2O_5 on solid supports has been developed because these reagents are easy to prepare and to handle and can be removed from the reaction mixture by simple filtration [5-12].

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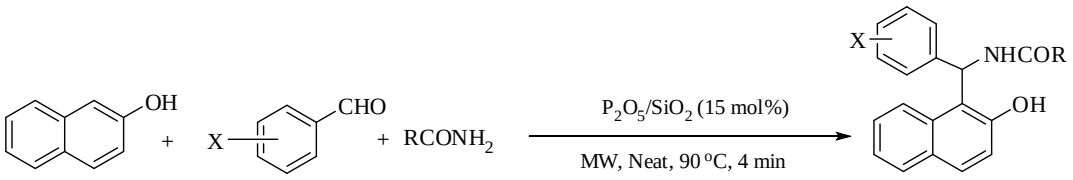
It is found that compounds containing 1,3-amino-oxygenated functional groups are frequently used as biologically active natural products and potent drugs such as nucleoside antibiotics and HIV protease inhibitors [13-16]. It is noteworthy that 1-amidoalkyl 2-naphthols can be converted to useful and important biological building blocks. For example, 1-amidoalkyl 2-naphthols can be hydrolyzed to 1-aminoalkyl 2-naphthol derivations that these compounds show hypotensive and bradycardiac effects [17, 18]. 1-Amidoalkyl 2-naphthols can be prepared by multicomponent condensation of aldehydes, 2-naphthols and acetonitrile or various amides in the presence of Lewis or Brönsted acids such as *p*-TSA [19], montmorillonite K10 [20], $Ce(SO_4)_2$ [21], Iodine [22], $Fe(HSO_4)_3$ [23], $Sr(OTf)_2$ [24], $K_5CoW_{12}O_{40}.3H_2O$ [25], sulfamic acid [26], molybdophosphoric acid [27], cation-exchange resins [28], silica sulfuric acid [29], $HClO_4$-SiO_2 [30], Brönsted acidic ionic liquid [31], and Thiamine hydrochloride [32]. Herein, we report an efficient, fast, and convenient procedure for the one-pot three-component synthesis of amidoalkyl naphthol derivatives from a variety of aromatic aldehydes, 2-naphthol and amides using catalytic amount of P_2O_5/SiO_2 under microwave irradiations (Scheme 1).

2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. The reactions were irradiated by using microwave laboratory system (Milestone, microsynth model, 1024). Melting points were measured with a Gallenkamp Apparatus and were uncorrected. IR



R = Me, Ph

X= H, Cl,Br, F, NO_2, Me, OMe, CN, MeOC(O)

Scheme 1.

spectra were obtained using a JASCO FT-IR-680 PLUS spectrometer. The ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer and a Bruker 500 MHz spectrometer with chemical shift (δ) values reported in ppm relative to an internal standard (TMS).

2.1. Preparation of Phosphorus Pentoxide on Solid Support

Phosphorus pentoxide (3 g) and 3 g of dried solid support were mixed for 10 min in a round bottomed flask until a fine and homogenous powder was obtained and then stored in a sealed flask for later using.

2.2. General Procedure for the Preparation of 1-Amidoalkyl 2-Naphthols

A magnetically stirred mixture of aldehyde (2 mmol), 2-naphthol (2 mmol), amide (2.4 mmol) and P_2O_5/SiO_2 (0.086 g, 15 mol %) was irradiated at 90 ºC by using a microwave laboratory system with the power level at 400 W for 4 min with 30 s/2 min intervals. The reaction was followed by TLC (EtOAc/cyclohexane, 1:3). After completion of the reaction, the reaction mixture was cooled to room temperature, and then the solid residue was dissolved in boiling EtOH and filtered to separate the catalyst. The solvent was evaporated by rotary evaporator and the crude product was purified by recrystallization from aqueous ethanol (25%).

2.3. General procedure for the synthesis of aryl or alkyl-14H-dibenzo[a,j]xanthenes

A magnetically stirred mixture of aldehyde (2 mmol), 2-naphthol (4 mmol) and P_2O_5/SiO_2 (0.086 g, 15 mol %) was irradiated at 100 ºC by using a microwave laboratory system with the power level at 400 W for 6 min with 30 s/3 min intervals. The reaction was followed by TLC (EtOAc/cyclohexane, 1:3). After completion of the reaction, the reaction mixture was cooled to room temperature, the product was extracted with chloroform and the crude product was recrystallized from ethanol to afford the pure 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*] xanthene derivatives.

The spectral data of some amidoalkyl naphthols

N-((2-hydroxynaphtalen-1-yl)(phenyl)methyl)acetamide (Table 2, entry 1): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 1.97 (s, 3 H, $COCH_3$), 7.11-7.16 (m, 4 H), 7.20-7.25 (m, 4 H), 7.33-7.37 (m, 1 H), 7.75-7.81 (m, 3 H), 8.44 (d, *J* = 8.0 Hz, 1 H, CH), 9.99 (s, 1 H, NH); IR (KBr, cm^{-1}): 3400, 3246, 1639,1516, 1437, 1338, 1278, 808, 742.

N-((2-chlorophenyl)(2-hydroxynaphtalen-1-yl)methyl) acetamide (Table 2, entry 2): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 1.90 (s, 3 H, $COCH_3$), 7.04 (d, *J* = 8.0 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 7.23-7.33 (m, 4 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 8.56 (d, *J* = 8.0 Hz, 1 H, CH), 9.80 (s, 1 H, NH); IR (KBr, cm^{-1}): 3419, 3065, 1656, 1514, 1439, 1334, 1271, 815, 752.

N-((2,6-dichlorophenyl)(2-hydroxynaphtalen-1-yl)methyl) acetamide (Table 2, entry 4): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 1.88 (s, 3 H, $COCH_3$), 7.0 (d, *J* = 8.8 Hz, 1 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 7.20 (t, *J* = 9.0 Hz, 1 H), 7.27-7.34 (m, 3 H), 7.47 (t, *J* = 8.0 Hz, 1 H), 7.72 (t, *J* = 8.8 Hz, 1 H), 7.81 (t, *J* = 8.4 Hz, 2 H), 8.60 (d, *J* = 8.8 Hz, 1 H, CH), 9.40 (s, 1 H, NH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 22.60,49.58,115.7,119.4, 122.38, 122.84, 127.30, 128.39, 128.62, 129.15, 129.49, 130.14, 133.14, 133.65,135.46, 137.97, 154.44, 168.75; IR (KBr, cm^{-1}): 3424, 3274, 1649, 1517, 1435, 1370, 1274, 822, 764, 741.

N-((4-bromophenyl)(2-hydroxynaphtalen-1-yl)methyl) acetamide (Table 2, entry 5): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 1.97 (s, 3 H, $COCH_3$), 7.04-7.09 (m, 3 H), 7.20 (d, *J* = 8.8 Hz, 1 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.36 (s, 1 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.75-7.81 (m, 2 H), 8.31 (s, 1 H), 8.46 (d, *J* = 8.0 Hz, 1 H, CH), 10.03 (s, 1 H, NH); IR (KBr, cm^{-1}): 3419, 3065, 1650, 1514, 1439, 1334, 1271, 813, 752.

N-((2-hydroxynaphtalen-1-yl)(4-nitrophenyl)methyl) acetamide (Table 2, entry 7): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 2.01 (s, 3 H, $COCH_3$), 7.16 (d, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 8.8 Hz, 1 H), 7.27 (t, *J* = 7.2 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 3 H), 7.81 (t, *J* = 8.8 Hz, 3 H), 8.13 (d, *J* = 8.8 Hz, 2 H), 8.59 (d, *J* = 8.0 Hz, 1 H, CH), 10.13 (s, 1 H, NH); IR (KBr, cm^{-1}): 3391, 3075, 1640, 1524, 1351, 1439, 1351, 1281, 853, 825, 752.

N-((2-hydroxynaphtalen-1-yl)(2,5-dimethoxyphenyl) methyl) acetamide (Table 2, entry 12): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 1.88 (s, 3 H, $COCH_3$), 3.48 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 6.73 (dd, J_1 = 8.6, J_2 = 2.8, Hz, 1 H), 6.79 (d, *J* = 8.8 Hz, 1 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 7.24 (t, *J* = 7.6 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.67 (d, *J* = 9.2 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 1 H), 8.33 (d, *J* = 8.4 Hz, 1 H,

CH), 9.81 (s, 1 H, NH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 23.11, 44.90, 55.72, 56.38, 111.47, 112.23, 116.3, 119.09, 119.37, 122.64, 123.84, 126.28, 128.62, 128.71, 129.20, 132.13, 133.03, 151, 21, 153.23, 153.72, 168.81; IR (KBr, cm^{-1}): 3365, 3173, 3003, 2834, 1644, 1496, 1437, 1278, 1219, 1053, 1027, 820, 752.

N-((4-cyanophenyl)(2-hydroxynaphtalen-1-yl)methyl) acetamide (Table 2, entry 13): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 2.0 (s, 3 H, $COCH_3$), 7.13 (d, *J* = 8.4 Hz, 1 H), 7.21 (d, *J* = 8.8 Hz, 1 H), 7.25-7.40 (m,4 H), 7.72 (d, *J* = 8.4 Hz, 2 H), 7.80 (t, *J* = 8.8 Hz, 3 H), 8.53 (d, *J* = 8.0 Hz, 1 H, CH), 10.09 (s, 1 H, NH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 23.0, 48.34, 109.26, 118.39, 118.86, 119.45, 123.03, 123.42, 127.12, 127.42, 128.89, 129.13, 130.26, 132.44, 132.67, 149.40, 153.79, 170.15; IR (KBr, cm^{-1}): 3380, 3075, 2958, 2231, 1629, 1510, 1439, 1333, 1280, 1247, 819, 753.

Methyl-4-(acetamido(2-hydroxynaphtalene-1-yl)methyl) benzoate (Table 2, entry 14): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 1.99 (s, 3 H, $COCH_3$), 3.80 (s, 3 H, OCH_3), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.19-7.38 (m, 5 H), 7.75-7.87 (m, 5 H), 8.51 (d, *J* = 8.0 Hz, 1 H, CH), 10.05 (s, 1 H, NH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 23.04, 48.27, 52.44, 118.80, 118.88, 122.95, 123.60, 126.73, 126.95, 127.95, 128.93, 129.07, 129.46, 130.06, 132.72, 149.14, 153.73, 166.60, 170.07; IR (KBr, cm^{-1}): 3388, 3249, 3064, 2955, 1710, 1647, 1516, 1438, 1281, 1114, 822, 746.

1-((4-Bromophenyl)(2-hydroxynaphtalene-1-yl)methyl) benzamide (Table 2, entry 17): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 7.18-7.33 (m, 4 H), 7.43-7.56 (m, 7 H), 7.77-7.87 (m, 4 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 9.02 (d, *J* = 8.0 Hz, 1 H, CH), 10.35 (s, 1 H, NH); ^{13}C NMR (100 MHz, DMSO-d_6,ppm) δ: 49.24, 118.29, 119.08, 120.04, 123.19, 127.32, 127.71, 128.84, 128.94, 129.19, 130.07, 131.50, 131.96, 132.69, 134.62, 141.99, 153.72, 166.38; IR (KBr, cm^{-1}): 3418, 3185, 1629, 1512, 1486, 1440, 1341, 1266, 811, 725.

1-((2-Hydroxynaphtalene-1-yl)(3-nitrophenyl)methyl) benzamide (Table 2, entry 19): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 7.25 (d, *J* = 8.8 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.53-7.60 (m, 3 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.84 (t, *J* = 7.2 Hz, 2 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 8.08-8.12 (m, 3 H), 9.16 (d, *J*: 8.0 Hz, 1 H, CH), 10.44 (s, 1 H, NH); IR (KBr, cm^{-1}): 3422, 3182, 1630, 1527, 1350, 1488, 1341, 1269, 810, 728.

1- ((2-Hydroxynaphtalene-1-yl) (2,5 -dimethoxyphenyl) methyl) benzamide (Table 2, entry 21): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 3.60 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 6.76 (dd, J_1 = 8.0 Hz, J_2 = 2.8 Hz, 1 H), 6.89 (d, *J* = 9.2 Hz, 1 H), 7.06 (s, 1 H), 7.17 (d, *J* = 8.8 Hz, 1 H), 7.27 (t, *J* = 8.8 Hz, 1 H), 7.41-7.51 (m, 5 H), 7.71-7.84 (m, 4 H), 8.23 (d, *J* = 8.4 Hz, 1 H), 8.83 (d, *J* = 8.8 Hz, 1 H, CH), 10.16 (s, 1 H, NH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 45.80, 55.66, 56.62, 111.19, 112.53, 116.52, 119.05, 119.24, 122.92, 123.71, 126.59, 127.63, 128.73, 128.81, 128.85, 129.41, 131.39, 131.65, 132.95, 135.07, 151.36, 153.34, 153.74, 165.47; IR (KBr, cm^{-1}): 3420, 3167, 2993, 2831, 1639, 1577, 1493, 1340, 1276, 1218, 1054, 814, 746.

The spectral data of some dibenzo [a,j] xanthenes

14-(2-Chlorophenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 2): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.85 (s, 1 H, CH), 6.93-6.99 (m, 2 H), 7.30 (d, *J* = 7.1 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.54 (d, *J* = 8.8 Hz, 2 H), 7.67 (t, *J* = 7.5 Hz, 2 H), 7.84 (d, *J* = 8.9 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 8.79 (d, *J* = 8.5 Hz, 2 H); IR (KBr, cm^{-1}): 3056, 1620, 1592, 1514, 1459, 1429, 1402, 1254, 1032, 964, 828, 810, 749, 739 .

14-(3-Chlorophenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 3): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.51 (s, 1 H, CH), 7.02 (d, *J* = 8.4 Hz, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 7.46-7.50 (m, 4 H), 7.53 (d, *J* = 8.9 Hz, 2 H), 7.65 (t, *J* = 7.1 Hz, 2 H), 7.85 (d, *J* = 8.9 Hz, 2 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 8.37 (d, *J* = 8.5 Hz, 2 H); IR (KBr, cm^{-1}): 3067, 1621, 1590, 1572, 1514, 1455, 1430, 1397, 1245, 1065, 959, 811, 755, 746.

14-(4-Chlorophenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 4): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.51 (s, 1 H, CH), 7.15 (d, *J* = 8.5 Hz, 2 H), 7.45-7.49 (m, 4 H), 7.52 (d, *J* = 8.9 Hz, 2 H), 7.61 (t, *J* = 7.3 Hz, 2 H), 7.85 (d, *J* = 8.9 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 8.36 (d, *J* = 8.5 Hz, 2 H); IR (KBr, cm^{-1}): 3025, 1620, 1590, 1483, 1457, 1400, 1239, 1082, 1012, 958, 831, 806, 740.

14-(4-Bromophenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 5): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.50 (s, 1 H, CH), 7.30 (d, *J* = 8.5 Hz, 2 H), 7.42-7.48 (m, 4 H), 7.52 (d, *J* = 8.9 Hz, 2 H), 7.63 (t, *J* = 7.2 Hz, 2 H), 7.85 (d, *J* = 8.9 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 8.36 (d, *J* = 8.5 Hz, 2 H); IR (KBr, cm^{-1}): 3068, 2905, 1620, 1590, 1481, 1456, 1430, 1400, 1238, 1072, 1008, 961, 826, 808, 739.

14-(3-Nitrophenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 7): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.60 (s, 1 H, CH), 7.29 (t, *J* = 7.7 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.55 (d, *J* = 8.9 Hz, 2 H), 7.66 (t, *J* = 7.7 Hz, 2 H), 7.84-7.88 (m, 6 H), 8.33 (d, *J* = 8.5 Hz, 2 H), 8.47 (s, 1 H); IR (KBr, cm^{-1}): 3080, 1621, 1592, 1529, 1458, 1430, 1401, 1347, 1251, 1140, 1081, 964, 825, 808, 744.

14-(4-Cyanophenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 9): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.57 (s, 1 H, CH), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 7.8 Hz, 2 H), 7.54 (d, *J* = 8.9 Hz, 2 H), 7.62-7.66 (m, 4 H), 7.87 (d, *J* = 8.9 Hz, 2 H), 7.89 (d, *J* = 8.2 Hz, 2 H), 8.31 (d, *J* = 8.50 Hz, 2 H); ^{13} C NMR (125 MHz, $CDCl_3$/DMSO-d_6, ppm) δ: 38.45, 110.74, 116.36, 118.46, 119.01, 122.51, 124.97, 127.56, 129.29, 129.46, 129.91, 131.48, 131.55, 132.81, 149.23, 150.43; IR (KBr, cm^{-1}): 3056, 2225, 1621, 1604, 1590, 1514, 1500, 1431, 1413, 1397, 1237, 1064, 954, 836, 808, 780, 738.

Methyl- 4-(14H-dibenzo[a.j] xanthenes-14-yl) benzoate (Table 4, entry 10): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 3.82 (s, 3 H, OCH_3), 6.55 (s, 1 H, CH), 7.45-7.48 (m, 2 H), 7.54 (d, *J* = 8.9 Hz, 2 H), 7.61-7.64 (m, 2 H), 7.66 (d, *J* = 8.5 Hz, 2 H), 7.84 (d, *J* = 8.9 Hz, 2 H), 7.86-7.89 (m, 4 H), 8.37 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 38.53, 52.36, 116.87, 118.45, 122.86, 124.82, 128.74, 129.32, 129.64, 130.31, 131.48, 131.73, 149.12, 150.42, 167.04; IR (KBr, cm^{-1}): 3060, 2996, 2948, 1707, 1591, 1512, 1457, 1431, 1402, 1288, 1250, 1241, 1189, 1115, 958, 818, 804, 746.

14-(4-Formylphenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 11): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.53 (s, 1 H, CH), 7.38 (t, *J* = 7.9 Hz, 2 H), 7.45 (d, *J* = 8.9 Hz, 2 H), 7.54 (t, *J* = 7.9 Hz, 2 H), 7.61 (d, *J* = 8.3 Hz, 2 H), 7.65 (d, *J* = 8.3 Hz, 2 H), 7.76-7.79 (m, 4 H), 8.29 (d, *J* = 8.5 Hz, 2 H), 9.73 (s, 1 H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6,ppm) δ: 38.51, 116.54, 118.37, 122.65, 124.84, 127.42, 129.23, 129.28, 129.71, 130.37, 131.36, 131.54, 149.05, 152.02, 191.85; IR (KBr, cm^{-1}): 3055, 2829, 2741, 1691, 1600, 1591, 1572, 1514, 1457, 1431, 1402, 1251, 1240, 1215, 1170, 963, 821, 806, 743, 671.

14-(4-Methylphenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 12): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 2.18 (s, 3 H, CH_3), 6.50 (s, 1 H, CH), 7.00 (d, *J* = 8.0 Hz, 2 H), 7.44-7.48 (m, 4 H), 7.53 (d, *J* = 8.9 Hz, 2 H), 7.63 (t, *J* = 7.0 Hz, 2 H), 7.83 (d, *J* = 8.9 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 8.44 (d, *J* = 8.5 Hz, 2 H); IR (KBr, cm^{-1}): 3019, 2901, 1620, 1590, 1508, 1457, 1429, 1401, 1247, 961, 808, 739, 609.

14-(4-Methoxyphenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 13): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 3.66 (s, 3 H, OCH_3), 6.49 (s, 1 H, CH), 6.71 (d, *J* = 8.8 Hz, 2 H), 7.43-7.47 (m, 4 H), 7.52 (d, *J* = 8.9 Hz, 2 H), 7.63 (t, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.9 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 8.43 (d, *J* = 8.5 Hz, 2 H); IR (KBr, cm^{-1}): 3072, 2833, 1591, 1457, 1430, 1399, 1248, 1177, 1027, 961, 830, 808, 741.

14-(3-Methoxyphenyl)-14H-dibenzo[a.j]xanthene (Table 4, entry 15): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 3.59 (s, 3 H, OCH_3), 6.42 (s, 1 H, CH), 6.48 (d, *J* = 8.2 Hz, 1 H), 7.04 (t, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.44 (d, *J* = 9.0 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 2 H), 7.71-7.82 (m, 4 H), 8.36 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 38.17, 55.23, 111.19, 115.16, 117.40, 118.23, 121.00, 122.94, 124.45, 127.00, 128.99, 129.07, 129.50, 131.27, 131.68, 145.01, 148.96, 159.97; IR (KBr, cm^{-1}): 3070, 3015, 2961, 2934, 2899, 1603, 1593, 1581, 1514, 1486, 1457, 1431, 1401, 1271, 1252, 1241, 1051, 964, 809, 775, 745.

2-(14H-dibenzo[a.j]xanthenes-14-yl)pyridine (Table 4, entry 16): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.76 (s, 1 H, CH), 6.91 (m, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 7.34 (m, 1 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.58 (t, *J* = 7.6 Hz, 2 H), 7.83 (d, *J* = 8.8 Hz, 4 H), 8.54 (d, *J* = 4.8 Hz, 1 H), 8.68 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 41.93, 116.00, 117.90, 121.23, 123.84, 123.99, 124.38, 126.92, 128.39, 129.18, 130.90, 131.92, 137.10, 147.74, 148.20, 164.70; IR (KBr, cm^{-1}): 3044, 1620, 1588, 1513, 1458, 1429, 1407, 1255, 1244, 1147, 967, 831, 805, 773, 754.

3-(14H-dibenzo[a.j]xanthenes-14-yl)pyridine (Table 4, entry 17): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 6.46 (s, 1 H, CH), 6.68 (d, *J* = 8.4 Hz, 2 H), 7.20 (m, 4 H), 7.42 (m, 4 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.58 (m, 2 H), 8.39 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 37.09, 113.84, 117.53, 117.99, 122.68, 124.20, 126.74, 128.71, 128.79, 129.14, 131.07, 131.41, 137.36, 148.68, 157.85; IR (KBr, cm^{-1}): 3060, 1591, 1509, 1457, 1430, 1399, 1249, 1177, 1029, 961, 830, 808, 742.

14-Isopropyl-14H-dibenzo[a.j]xanthene (Table 4, entry 19): ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 0.88 (d, *J* = 6.9 Hz, 6 H), 2.33 (m, 1 H), 5.50 (d, *J* = 3.8 Hz, 1 H), 7.47 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 7.1 Hz, 2 H), 7.64 (t, *J* = 6.9 Hz, 2 H), 7.83 (d, *J* = 8.8 Hz, 2 H), 7.91 (d, *J* = 8.1 Hz, 2 H), 8.35 (d, *J* = 8.5 Hz, 2 H); IR (KBr, cm^{-1}): 3068, 2959, 1590, 1515, 1456, 1432, 1398, 1250, 1237, 955, 815,739.

3. Results and Discussion

Because of its avidity for water, P_2O_5 widely used as a dehydrating agent, but its efficacy as a desiccant is greatly impaired by the formation of a crusty surface film of hydrolysis products unless it is finely dispersed on glass wool [33]. The main reason of this observation is due to the hydroxyl groups on the surface of the glass wool. It is known that changing a support may completely alter the course of reaction or prevent catalysis [34]. Therefore, the careful choice of a support is frequently critical if satisfactory results in a synthetic application are to be achieved. By following these results, we tried to find the best solid support for P_2O_5 in the synthesis of 1-amidoalkyl 2-naphthols. Thus, the reaction of 2-naphthol (2 mmol), 3-nitrobenzaldehyde (2 mmol) and acetamide (2.4 mmol) was studied as a simple model using catalytic amount of P_2O_5 (15 mol%) on various mineral supports (Table 1). It was found that supported P_2O_5 on SiO_2 afforded better result. It may be due to high surface area of SiO_2 (300-600 $m^2.g^{-1}$) [34] leading to improvements in its reactivity. Moreover, a large number of hydroxyl groups on SiO_2 that the majority of them react with P_2O_5 leading to stabilization of P_2O_5 [10]. In addition, SiO_2 is nontoxic, inexpensive, widely available and useful in straightforward work-up procedures. After optimization of the support, to develop the reaction conditions, we also studied this reaction by using microwave irradiation under solvent-free conditions. It was found that the best result was obtained when the reaction was carried out in the presence of P_2O_5/SiO_2 (0.086 g, 15 mol%) under microwave irradiation (Table 1, entry 6). Moreover, using microwave irradiation, the present reaction was studied with SiO_2 alone (0.043 g) under the same conditions (Table 1, entry 7), it was observed that the

Table 1. Reactivity of P_2O_5 (0.043 g, 15 mol %) on support (0.043 g) for the reaction of 2-naphthol, acetamide and 3-nitrobenzaldehyde under solvent-free conditions[a].

Entry	Support	Time (min)	Yield (%) [b]
1	SiO_2	25	87
2	Acidic alumina	25	85
3	Montmorillonite	25	81
4	ZSM-5	25	78
5	TiO_2	25	72
6 [c]	SiO_2	4	92
7 [c,d]	SiO_2	4	10
8 [c,e]	-	4	80
9 [c,f]	-	4	trace

[a] The reaction was carried out at 110 º C.

[b] The yields refer to the isolated pure products.

[c] The reaction was carried out under microwave irradiation at 90 º C.

[d] The reaction was carried out with SiO_2 alone without using P_2O_5.

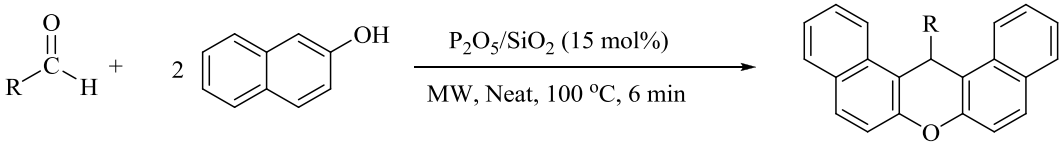
[e] The reaction was carried out with P_2O_5 alone without using SiO_2.

[f] The reaction was carried out without using catalyst.

corresponding product was obtained in low yield (10 %). To evaluate the role of SiO_2, as a support, we studied the present reaction in the absence of SiO_2 using P_2O_5 alone (0.043 g). It was found that the yield by using P_2O_5/SiO_2 were greater than those with P_2O_5 alone under the same conditions (Table 1, entry 8). Using SiO_2 as a support not only increases the reaction rate but also minimizes cross contamination between the product and phosphoric acid generated during the course of the reaction [9, 10, 34]. In the absence of the catalyst, the reaction was carried out in trace yield under the same conditions (Table 1, entry 9). Using 15 mol % of the catalyst was sufficient to progress the reaction and an increase of the catalyst amount did not improve the yield.

Using this method, different kinds of aromatic aldehydes reacted with amides and 2-naphtol to produce the corresponding 1-aminoalkyl 2-naphthol derivatives under solvent-free conditions (Table 2). Several aromatic aldehydes with different functional groups were subjected to the condensation reaction and the desire products were synthesized in good to high yields and short reaction times. The substituted functional groups on the aromatic ring of the aldehyde did not remarkably effect on the yields and reaction times. In addition, we did not observe the steric effect of *ortho*-substituents on the reaction time and yield.

We also studied the synthesis of benzoxanthens using phosphorus pentoxide on solid support (Scheme 2). It is known that Xanthenes, especially benzoxanthens, are important intermediates in organic synthesis due to their wide range of biological and therapeutic properties [35-37]. Moreover, these compounds can be used as dyes [38], pH-sensitive fluorescent materials for visualization of biomolecules [39] and in laser technology [40]. The reported methods for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*] xanthenes involve the mixing of 2-naphthol with aldehydes in the presence of an acidic catalyst such as *p*-TSA [41], LiBr [42], Amberlyst-15 [43], silica sulfuric acid [44, 45], molecular iodine [46, 47], sulfamic acid [48], heteropoly acid [49,50], $Yb(OTf)_3$ [51], alum [52], $BF_3.SiO_2$ [53], Montmorillonite K10 [54], and Ionic liquids [55-59]. Initially, to find the best solid support for P_2O_5 in the synthesis of benzoxanthens, the reaction between 2-naphthol (4 mmol) and benzaldehyde (2 mmol) was followed as a simple model using catalytic amount of P_2O_5 (15 mol%) on various mineral supports (Table 3). It was found that supported P_2O_5 on SiO_2 provided the best result under



R = $CH_3CH_2CH_2$, $(CH_3)_2CH$, 2-Pyridyl, 3-Pyridyl, Substitiuted phenyl

Scheme 2.

Table 2. Preparation of 1-amidoalkyl 2-naphthols from aryl aldehydes, amides and 2-naphthol by using catalytic amount of P_2O_5/SiO_2 under microwave irradiation[a].

Entry	Aldehyde	Amides R	Yield (%)[b]	mp (°C)	
				Found	Reported [Ref]
1	C_6H_5CHO	CH_3	87	240-242	245-246[30]
2	2-ClC_6H_4CHO	CH_3	89	196-198	194-196[26]
3	4-ClC_6H_4CHO	CH_3	90	222-224	223-225[30]
4	2,6-$Cl_2C_6H_3CHO$	CH_3	85	222-224	223-224[31]
5	4-BrC_6H_4CHO	CH_3	87	228-230	229-231[31]
6	3-$O_2NC_6H_4CHO$	CH_3	92	241-242	241-242[30]
7	4-$O_2NC_6H_4CHO$	CH_3	88	226-228	222-223[31]
8	4-FC_6H_4CHO	CH_3	87	200-202	203-205[26]
9	4-MeC_6H_4CHO	CH_3	86	214-217	214-216[31]
10	3-$MeOC_6H_4CHO$	CH_3	85	222-224	218-220[31]
11	4-$MeOC_6H_4CHO$	CH_3	82	179-181	183-185[30]
12	2,5-$(MeO)_2C_6H_3CHO$	CH_3	81	230-232	228-230[31]
13	4-NCC_6H_4CHO	CH_3	90	236-238	232-234[31]
14	4-$CH_3OCOC_6H_4CHO$	CH_3	89	223-225	225-227[31]
15	C_6H_5CHO	C_6H_5	85	233-235	234-236[31]
16	3-$MeOC_6H_4CHO$	C_6H_5	84	214-216	214-216[31]
17	4-BrC_6H_4CHO	C_6H_5	83	180-182	182-184[31]
18	4-ClC_6H_4CHO	C_6H_5	84	181-182	180-182[31]
19	3-$O_2NC_6H_4CHO$	C_6H_5	85	230-232	233-235[31]
20	4-MeC_6H_4CHO	C_6H_5	83	211-213	209-211[31]
21	2,5-$(MeO)_2C_6H_3CHO$	C_6H_5	82	240-242	238-240[31]

[a]The yields refer to the isolated pure products which were characterized from their spectral data and were compared with authentic samples.

[b]The yields refer to the isolated pure products.

microwave irradiation. After optimization of the reaction conditions, we studied the generality of these conditions to other substrates. Using this method, different kinds of aromatic and aliphatic aldehydes were reacted with 2-naphtol to produce the corresponding 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes under microwave irradiation (Table 4). Several aromatic aldehydes with different functional groups were subjected to the condensation reaction and the desire products were synthesized in good to high yields and short reaction times. The substituted functional groups on the aromatic ring of the aldehyde affected on the yields of the products. In comparison with electron with-drawing groups on the aromatic aldehydes, we found that the presence of electron donating groups decreased the yields of the products (Table 4, entries 13-15). It was found that hetero aromatic aldehydes and also aliphatic aldehydes reacted with 2-naphtol respectively and the corresponding products were obtained in good yields (Table 4, entries 16-19). We also studied the reaction between terephthaldialdehyde (1 mmol) and excess amount of 2-naphtol (4 mmol), we expected that both of the formyl groups on the aromatic ring of terephthaldialdehyde would react with 2-naphtol. However, we observed that one of the formyl groups were condensed with 2-naphtol and another group was intact because of steric effects between *o*-hydrogens of benzene ring and the xanthene ring [54] (Scheme 3). Finally, to evaluate the present work in

Table 3. Reactivity of P_2O_5 (0.043 g, 15 mol %) on support (0.043 g) for the reaction of 2-naphthol and benzaldehyde under solvent-free conditions.

Entry	Support	Time (min)	Yield (%) [b]
1	SiO_2	90	85
2	Acidic alumina	90	83
3	Montmorillonite	90	82
4	ZSM-5	90	79
5	TiO_2	90	75
6 [c]	SiO_2	6	88

[a]The reaction was carried out at 125 ° C.

[b]The reaction was carried out under microwave irradiation at 100ºC.

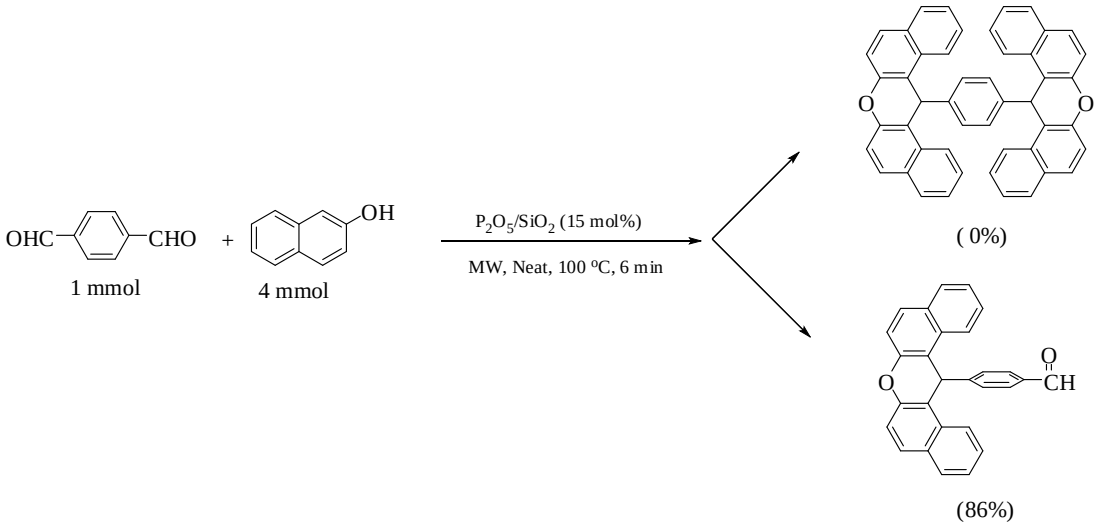
[c]The yields refer to the isolated pure products.

Table 4. Preparation of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes using catalytic amount of P_2O_5/SiO_2 under microwave irradiation[a].

Entry	Aldehyde	Yield (%)[b]	mp (°C)	
			Found	Reported [Ref]
1	Benzaldehyde	88	183-184	183-184[53]
2	2-Chlorobenzaldehyde	91	212-214	214-216[53]
3	3-Chlorobenzaldehyde	94	210-211	209-211[53]
4	4-Chlorobenzaldehyde	93	288-290	289-290[53]
5	4-Bromobenzaldehyde	92	296-298	297-298[53]
6	4-Fluorobenzaldehyde	91	239-241	238-240[53]
7	3-Nirtobenzaldehyde	94	210-212	210-211[53]
8	2-Nirtobenzaldehyde	92	213-215	214-215[53]
9	4-Cyanobenzaldehyde	89	291-293	291-292[51]
10	Methyl 4-formylbenzoate	88	249-251	249-250[58]
11	Terephthaldialdehyde	86	307-309	308-312[54]
12	4-Methylbenzaldehyde	85	226-228	227-228[53]
13	4-Methoxybenzaldehyde	81	202-204	203-205[53]
14	2-Methoxybenzaldehyde	78	256-258	258-259[53]
15	3-Methoxybenzaldehyde	83	175-177	174-176[58]
16	2-Pyridinecarbaldehyde	62	236-237	235-237[58]
17	3-Pyridinecarbaldehyde	68	200-202	200-202[59]
18	Butyraldehyde	81	152-154	152-154[53]
19	Isobutyraldehyde	78	152-154	155-157[53]

[a]The yields refer to the isolated pure products which were characterized from their spectral data and were compared with authentic samples.
[b]The yields refer to the isolated pure products.

comparison with recently reported ones, we compared our results with a number of catalysts. As shown in Table 5, 6, the results show that the reaction yields are compatible with the reported ones and this reagent (P_2O_5/SiO_2) is superior to other reagents in view of the lowest reaction time.



Scheme 3.

Table 5. Comparison of P_2O_5/SiO_2 with various catalysts for the reaction of 2-naphthol, acetamide and a number of aldehydes.

Entry	Aldehyde	Catalyst (mol%) /Temp/Conditions	Time	Yield (%)	Ref
1	PhCHO	*P*-TSA (10) /125 °C/Neat	4 h	90	[19]
2	PhCHO	Montmorillonite K10 (0.1 g) /125 °C/Neat	1.5 h	89	[20]
3	PhCHO	I_2 (5) /125 °C/Neat	5.5 h	85	[22]
4	PhCHO	$Fe(HSO_4)_3$ (5) /85 °C/Neat	65 min	83	[23]
5	PhCHO	$K_5CoW_{12}O_{40}.3H_2O$ (1) /125 °C/Neat	2 h	90	[25]
6	PhCHO	Sulfamic acid (50) /28-30 °C/Neat, sonication	15 min	89	[26]
7	PhCHO	$HClO_4$-SiO_2 (0.6) /110 °C/Neat	40 min	89	[30]
8	PhCHO	P_2O_5/SiO_2 (15) /90 °C/Neat, MW	4 min	87	-
9	4-MeOPhCHO	$Fe(HSO_4)_3$ (5) /85 °C/Neat	55 min	84	[23]
10	4-MeOPhCHO	$HClO_4$-SiO_2 (0.6) /110 °C/Neat	45 min	86	[30]
11	4-MeOPhCHO	P_2O_5/SiO_2 (15) /90 °C/Neat, MW	4 min	82	-
12	4-ClPhCHO	*P*-TSA (10) /125 °C/Neat	4 h	90	[19]
13	4-ClPhCHO	$Fe(HSO_4)_3$ (5) /85 °C/Neat	45 min	88	[23]
14	4-ClPhCHO	Sulfamic acid (50) /28-30 °C/DCE, sonication	2 h	92	[26]
15	4-ClPhCHO	$HClO_4$-SiO_2 (0.6) /110 °C/Neat	40 min	93	[30]
16	4-ClPhCHO	P_2O_5/SiO_2 (15) /90 °C/Neat, MW	4 min	90	-
17	3-NO_2PhCHO	*P*-TSA (10) /125 °C/Neat	4 h	90	[19]
18	3-NO_2PhCHO	Montmorillonite K10 (0.1 g) /125 °C/Neat	30 min	96	[20]
19	3-NO_2PhCHO	I_2 (5) /125 °C/Neat	5 h	81	[22]
20	3-NO_2PhCHO	$Fe(HSO_4)_3$ (5) /85 °C/Neat	25 min	97	[23]
21	3-NO_2PhCHO	$K_5CoW_{12}O_{40}.3H_2O$ (1) /125 °C/Neat	3 h	78	[25]
22	3-NO_2PhCHO	Sulfamic acid (50) /28-30 °C/DCE, sonication	1.5 h	93	[26]
23	3-NO_2PhCHO	$HClO_4$-SiO_2 (0.6) /110 °C/Neat	30 min	95	[30]
24	3-NO_2PhCHO	P_2O_5/SiO_2 (15) /90 °C/Neat, MW	4 min	92	-
25	2-ClPhCHO	$Fe(HSO_4)_3$ (5) /85 °C/Neat	50 min	86	[23]
26	2-ClPhCHO	Sulfamic acid (50) /28-30 °C/Neat, sonication	25 min	89	[26]
27	2-ClPhCHO	$HClO_4$-SiO_2 (0.6) /110 °C/Neat	70 min	87	[30]
28	2-ClPhCHO	P_2O_5/SiO_2 (15) /90 °C/Neat, MW	4 min	89	-

4. Conclusion

In summary, we introduced P_2O_5/SiO_2 as an inexpensive, easily available, non-corrosive and environmentally benign atalyst. In this work, we reported a facile, convenient and solvent-free method for the one-pot synthesis of amidoalkyl naphthols by condensation of aromatic aldehydes with amides and 2-naphthol in the presence of P_2O_5/SiO_2 as an efficient catalyst. Moreover, we exposed a convenient, efficient and practical procedure for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*] xanthenes in good yields and short. reaction times using catalytic amount of P_2O_5/SiO_2. The notable advantages of this methodology were operational simplicity, availability of the reactants, short reaction times, high yields and easy work-up.

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Table 6. Comparison of P_2O_5/SiO_2 with various catalysts for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes using 2-naphthol and various aldehydes.

Entry	Aldehyde	Catalyst (mol%) /Temp/Conditions	Time	Yield (%)	Ref
1	PhCHO	*P*-TSA (2) /125 °C/Neat	4 h	89	[41]
2	PhCHO	SiO_2-SO_3H (13) /125 °C/Neat	20 min	90	[45]
3	PhCHO	I_2 (25) /125 °C/Neat	20 min	90	[46]
4	PhCHO	Sulfamic acid (10) /125 °C/Neat	8 h	93	[48]
5	PhCHO	$Yb(OTf)_3$ (1) /110 °C/Ionic liquid ([BPy]BF_4)	7 h	89	[51]
6	PhCHO	$BF_3.SiO_2$ (0.8 g) /60 °C/$CHCl_3$, sonication	6 min	95	[53]
7	PhCHO	P_2O_5/SiO_2 (15) /100 °C/Neat, MW	6 min	88	-
8	4-MeOPhCHO	*P*-TSA (2) /125 °C/Neat	6 h	80	[41]
9	4-MeOPhCHO	I_2 (25) /125 °C/Neat	15 min	92	[46]
10	4-MeOPhCHO	Sulfamic acid (10) /125 °C/Neat	10 h	92	[48]
11	4-MeOPhCHO	$Yb(OTf)_3$ (1) /110 °C/Ionic liquid ([BPy]BF_4)	6 h	95	[51]
12	4-MeOPhCHO	$BF_3.SiO_2$ (0.8 g) /60 °C/$CHCl_3$, sonication	6 min	91	[53]
13	4-MeOPhCHO	P_2O_5/SiO_2 (15) /100 °C/Neat, MW	6 min	81	-
14	4-ClPhCHO	*P*-TSA (2) /125 °C/Neat	2.5 h	95	[41]
15	4-ClPhCHO	I_2 (25) /125 °C/Neat	15 min	93	[46]
16	4-ClPhCHO	Sulfamic acid (10) /125 °C/Neat	7 h	95	[48]
17	4-ClPhCHO	$Yb(OTf)_3$ (1) /110 °C/Ionic liquid ([BPy]BF_4)	5 h	89	[51]
18	4-ClPhCHO	SiO_2-SO_3H (13) /125 °C/Neat	25 min	87	[45]
19	4-ClPhCHO	P_2O_5/SiO_2 (15) /100 °C/Neat, MW	6 min	93	-
20	3-NO_2PhCHO	*P*-TSA (2) /125 °C/Neat	2.5 h	90	[41]
21	3-NO_2PhCHO	Sulfamic acid (10) /125 °C/Neat	12 h	91	[48]
22	3-NO_2PhCHO	SiO_2-SO_3H (13) /125 °C/Neat	70 min	85	[45]
23	3-NO_2PhCHO	$BF_3.SiO_2$ (0.8 g) /60 °C/$CHCl_3$, sonication	6 min	93	[53]
24	3-NO_2PhCHO	P_2O_5/SiO_2 (15) /100 °C/Neat, MW	6 min	94	-
25	2-ClPhCHO	*P*-TSA (2) /125 °C/Neat	2.5 h	88	[41]
26	2-ClPhCHO	I_2 (25) /125 °C/Neat	15 min	90	[46]
27	2-ClPhCHO	Sulfamic acid (10) /125 °C/Neat	8 h	90	[48]
28	2-ClPhCHO	P_2O_5/SiO_2 (15) /100 °C/Neat, MW	6 min	91	-
29	$CH_3(CH_2)_2CHO$	$BF_3.SiO_2$ (0.8 g) /60 °C/$CHCl_3$, sonication	6 min	88	[53]
30	$CH_3(CH_2)_2CHO$	P_2O_5/SiO_2 (15) /100 °C/Neat, MW	6 min	81	-

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