Catalytic application of two novel sandwich-type polyoxometalates in synthesis of 14-substituted-14*H*-dibenzo[*a*, *j*]xanthenes

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Abstract. Two sandwich-type polyoxometalates $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ and $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ were found to be as novel efficient catalysts for one-pot synthesis of various 14-aryl or alkyl-14*H*-dibenzo[*a*, *j*]xanthenes. Three-component condensation reactions of β-naphthol with aromatic or aliphatic aldehydes in the presence of these catalysts were investigated. These reactions were studied under different conditions such as solvent-free media using both conventional heating and microwave irradiation and also several solvents. Results showed that the optimum reaction time and the yield were obtained when reactions were carried out under solvent-free conditions. Furthermore, the catalysts could be recovered conveniently and reused efficiently.

Keywords. 14-Substituted-14*H*-dibenzo[*a*, *j*]xanthenes; sandwich polyoxometalates; catalyst; solvent-free.

1. Introduction

Polyoxometalates (POMs) are well-known inorganic metal oxygen cluster species have been attracting more interest in diverse fields such as catalysis, medicine, analytical chemistry and magnetism.[1–6] The evolution of POMs chemistry is dependent on the preparation of novel polyoxoanions possessing unique structures and properties. POMs are formed by the early transition metals of groups V and VI in their highest oxidation states by condensation reactions in aqueous, acidic medium. The commonly used POMs building blocks still largely focus on the well-known Keggin,[7] Wells–Dawson,[8] Anderson,[9] Silverton[10] and Lindquist-type[11] anions.

The sandwich-type polyoxometalates obtained by reaction of the lacunary polyoxoanions with the transition-metal cations, are the excellent building blocks.[12] Up to now, numerous sandwich-type polyoxometalates have been prepared and mostly belong to the well-known Weakly ([$M_4(X_2W_{15}O_{56})_2]^{n-}$ and [$M_4(H_2O)_2(XW_9O_{34})_2]^{n-}$), Herve [$M_3(H_2O)_3(\alpha$-$XW_9O_{33})_2]^{n-}$ (M = transition metal, X = As^{III}, Sb^{III}, Se^{IV}, Bi^{III}) and Knoth-type [$M_3(A$-$XW_9O_{34})_2]^{n-}$ (X = P and Si) sandwich-type structures.[13–15] This type of compounds has attracted special interest on their potential application as catalyst.[16,17]

Xanthenes especially benzoxanthenes, are an important class of biologically active heterocycles with potential application as antibacterial,[18] antiviral agents.[19]

They are also candidates in photodynamic therapy (PDT).[20,21] Furthermore, benzoxanthenes are used as dyes,[22] in laser technologies[23] and in fluorescent materials.[24]

The synthesis of 14*H*-dibenzo[*a*, *j*]xanthenes is generally achieved by dehydration of *bis*(2-hydroxy-1-naphthyl) methane using POCl$_3$[25] or by boiling acetic acid diester of *bis*(2-hydroxy-1-naphthyl) methane,[26] the reaction β-naphthol with formamide and carbon monoxide.[27,28] However, those methods suffer from significant limitations, such as low yields of products, the need for a prolonged reaction time (from 16 h to 5 days), large quantities of solvent and catalyst involved, and harsh reaction conditions. Recently, benzoxanthenes was obtained by the condensation reaction between β-naphthol with aliphatic or aromatic aldehydes in the presence of hydrochloric acid or phosphoric acid,[29] sulphuric acid,[30] *p*-toluenesulphonic acid,[31] sulphamic acid,[32] Amberlyst-15,[33] HClO$_4$-SiO$_2$,[34] Dowex-50W,[35] Yb(OTf)$_3$,[36] alum,[37] Montmorillonite K-10,[38] heteropoly acid,[39] P$_2$O$_5$ or InCl$_3$[40] and indion-130[41] as catalyst.

It is to be noted that no published reports are available on open-access literatures on the use of the sandwich-type polyoxometalates as catalyst in the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*, *j*]xanthenes. In this study, an attempt was made to explain a facile and efficient synthetic strategy for synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*, *j*]xanthenes using one-pot condensation of β-naphthol with wide variety of aldehydes

in the presence of catalyst. Two sandwich-type poly-oxomatalates such as $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ and $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ as novel recyclable catalysts were used.

2. Experimental

2.1 *Materials and apparatus*

All chemicals were obtained from Merck and Romil was used without further purification. All yields were referred to isolated products after purification. Products were characterized by comparison with authentic samples by TLC, spectral and physical data. Melting points were determined on Electrothermal 9100 apparatus and were uncorrected. IR spectra were recorded on a Bruker Tensor 27 spectrometer with KBr plates. ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively in $CDCl_3$ solvent. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV. Elemental analysis (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The reaction was irradiated using microwave oven with controlled timer. The purity of the substances and the progress of the reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel 60F containing the fluorescent indicator UV254.

2.2 *Preparation of $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ catalyst*

The detailed procedure of preparation of $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ catalyst was reported elsewhere.[42] In brief, the solution of 14.85 g $Na_2WO_4\cdot$ $2H_2O$ (0.045 mol) and 1.58 g $Na_2HAsO_4\cdot7H_2O$ (0.005 mol) in water (50 mL) was added in a small portion to a solution containing 5.27 g $UO_2(NO_3)_2\cdot6H_2O$ (0.010 mol) and HNO_3 6.4 M (8.600 mL) in water (55 mL) and the resulting solution was refluxed for 2 h. Then, the solution was filtered off and 20 g KNO_3 (0.200 mol) was added to the filtrate. The resulting precipitate was filtered off, redissolved in hot water and reprecipitated with the addition of 10 g KNO_3 (0.100 mol). Consequently, the resulting solid was recrystallized from hot water.[42]

2.3 *Preparation of $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ catalyst*

The experimental procedure for preparation of $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ was similar to $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ with a replacement of $UO_2(NO_3)_2\cdot6H_2O$ by $Cu(NO_3)_2\cdot3H_2O$.

2.4 *Synthesis of 14-aryl or alkyl-14H-dibenzo[a, j] xanthenes in presence of catalysts under solvent condition*

A mixture of an aldehyde (1 mmol), 0.28 g β-naphthol (2 mmol) and 0.05 g $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ (0.013 mmol, 1.3 mol%) or 0.05 g $K_{12}[As_2W_{18}U_3O_{74}]\cdot$ $21H_2O$ (0.008 mmol, 0.8 mol%) in solvent (10 mL) was stirred at reflux for appropriate time (table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and the organic solvent was concentrated in vacuum to afford crude product. The crystalline pure product was obtained by further recrystalization from ethanol.

Table 1. The reaction between 4-fluorobenzaldehyde and β-naphthol using $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ (I) and $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ (II) catalysts under different conditions.

			I	II
Entry	Solvent	Conditions	Time (h)/Yield (%)[a]	Time (h)/Yield (%)[a]
1	Methanol	Reflux	10.00/trace	10.00/trace
2	$ClCH_2CH_2Cl$	Reflux	10.00/trace	10.00/trace
3	H_2O	Reflux	10.00/32	10.00/40
4	DMF	Reflux	10.00/trace	10.00/trace
5	Solvent-free	60°C	10.00/trace	10.00/20
6	Solvent-free	80°C	8.00/25	6.30/36
7	Solvent-free	100°C	5.30/53	4.00/60
8	Solvent-free	125°C	2.30/95	2.00/94
9	Solvent-free	140°C	10.00/trace	5.00/trace
10	Solvent-free/MW	900 W	15.30 min/90	8.00 min/93

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

2.5 Synthesis of 14-aryl or alkyl-14H-dibenzo[a, j] xanthenes in presence of catalysts under solvent-free condition by conventional heating

The molar composition of aldehyde, β-naphthol and catalysts were similar to solvent condition procedure. This mixture was heated under solvent-free at 125°C with stirring. After completion of reaction (monitored by TLC) the mixture was cooled and extracted with ethyl acetate. The organic layer was oven-dried over Na_2SO_4 and evaporated to give the crude product, which was recrystallized from ethanol to afford pure products.

2.6 Synthesis of 14-aryl or alkyl-14H-dibenzo[a, j] xanthenes in presence of catalysts under solvent-free condition by microwave irradiation

This reaction was carried out similar to solvent condition procedure in terms of molar composition. The mixture was taken in a glass vial and irradiated (900 W) for appropriate time. After completion of reaction (monitored by TLC), the products were purified similar to method conventional heating to give pure products.

2.7 Characterization of 14-aryl or alkyl-14H-dibenzo [a, j]xanthenes

All the products obtained were characterized by spectroscopic methods such as IR, NMR (^{1}H and ^{13}C), mass and elemental analysis. The spectral and analytical data of some representative aryl and alkyl 14H-dibenzo[a, j]xanthenes are presented below.

2.7a 14-Phenyl-14H-dibenzo[a, j]xanthenes (3a): Colourless solid. m.p.: 183–185°C, IR (KBr): $\overline{v}$ = 3074, 2886, 1621, 1592, 1514, 1490, 1456, 1402, 1252, 1079, 1027, 963, 827, 744, 700 cm^{-1}; ^{1}HNMR (500 MHz, CDCl$_3$): δ = 8.44 (2H, d, J = 8.45 Hz), 7.87 (2H, d, J = 7.9 Hz), 7.83 (2H, d, J = 8.85 Hz), 7.63 (2H, t, J = 7.7 Hz), 7.58 (2H, d, J = 8.3 Hz), 7.53(2H, d, J = 8.85 Hz), 7.45 (2H, t, J = 7.9 Hz), 7.19 (2H, t, J = 7.55 Hz), 7.03 (1H, t, J = 7.4 Hz), 6.5 (1H, s); ^{13}CNMR (125 MHz, CDCl$_3$): δ = 149.1, 145.4, 131.8, 131.4, 129.3, 129.2, 128.8, 128.6, 127.1, 126.7, 124.6, 123.1, 118.4, 117.7, 38.4 ppm; MS (70 eV): m/z = 358 (M$^+$, 22.5), 281 (100), 252 (13.3), 77 (4.4), Anal. Calcd. for $C_{27}H_{18}O$: C, 90.50; H, 5.02, Found: C, 90.44; H, 5.08.

2.7b 14-(4-Nitrophenyl)-14H-dibenzo[a, j]xanthene (3b): Yellow solid. m.p.: 311–312°C, IR (KBr): $\overline{v}$ = 3068, 2926, 1623, 1591, 1513, 1457, 1399, 1340, 1240, 1140, 1106, 1014, 959, 851, 827, 807, 744, 695 cm^{-1}; ^{1}HNMR (500 MHz, CDCl$_3$): δ = 8.29 (2H, d, J = 8.4 Hz), 7.95 (2H, d, J = 8.6 Hz), 7.88 (2H, d, J = 4.2 Hz), 7.83 (2H, d, J = 5.4 Hz), 7.67 (2H, d, J = 8.8 Hz), 7.61 (2H, t, J = 5.6 Hz), 7.50 (2H, d, J = 8.9 Hz), 7.44 (2H, t, J = 7.9 Hz), 6.65 (1H, s); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 152.6, 148.1, 145.9, 135.1, 130.8, 130.6, 129.6, 128.7, 127.2, 124.7, 123.8, 123.3, 117.8, 116.5, 36.8 ppm; MS (70 eV): m/z = 403 (M$^+$, 6.5), 281 (100), 252 (17.4), 69 (53.5). Anal. Calcd. for $C_{27}H_{17}NO_3$: C, 80.39; H, 4.21; N, 3.47, Found: C, 80.40; H, 4.47; N, 3.20.

2.7c 14-(4-Fluorophenyl)-14H-dibenzo[a, j]xanthene (3c): White solid. m.p.: 239–240°C, IR (KBr): $\overline{v}$ = 3068, 2927, 1623, 1593, 1501, 1457, 1432, 1397, 1245, 1212, 1157, 1081, 958, 831 cm^{-1}; ^{1}HNMR (500 MHz, CDCl$_3$): δ = 8.38 (2H, d, J = 8.5 Hz), 7.88 (2H, d, J = 8.05 Hz), 7.84 (2H, d, J = 8.9 Hz), 7.64 (2H, t, J = 7.55), 7.53 (2H, d, J = 8.75 Hz), 7.51–7.46 (4H, m), 6.87 (2H, d, J = 8.7 Hz), 6.52 (1H, s); ^{13}CNMR (125 MHz, CDCl$_3$): δ = 148.7, 131.3, 131, 129.6, 129.5, 129, 128.9, 126.8, 124.3, 122.4, 118, 117.1, 115.4, 115.2, 37.1 ppm; MS (70 eV): m/z = 376 (M$^+$, 72.2), 281 (100), 252 (22.5), 178 (6.7), 75(3.5); Anal. Calcd. for $C_{27}H_{17}FO$: C, 86.17; H, 4.52, Found: C, 86.57; H, 4.59.

2.7d 14-(4-Methylphenyl)-14H-dibenzo[a, j]xanthene (3f): White solid. m.p.: 227–229°C, IR (KBr): $\overline{v}$ = 3070, 2919, 1620, 1590, 1511, 1457, 1429, 1398, 1245, 1139, 1080, 960, 836, 811, 778, 740 cm^{-1}; ^{1}HNMR (500 MHz, CDCl$_3$): δ = 8.44 (2H, d, J = 8.55 Hz), 7.86 (2H, d, J = 8.05 Hz), 7.82 (2H, d, J = 8.85 Hz), 7.62 (2H, t, J = 8.2 Hz), 7.53 (2H, d, J = 8.85 Hz), 7.47–7.43 (4H, m), 7.00 (2H, d, J = 7.9 Hz), 6.5 (1H, s), 7 (3H, s); ^{13}CNMR (125 MHz, CDCl$_3$): δ = 149.1, 142.5, 136.2, 131.8, 131.5, 129.5, 129.2, 129.1, 128.5, 127.1, 124.6, 123.1, 118.4, 117.8, 38, 21.2 ppm; MS (70 eV): m/z = 372 (M$^+$, 12.5), 281 (100), 252 (15), 69 (37.5); Anal. Calcd. for $C_{28}H_{20}O$: C, 90.32; H, 5.37, Found: C, 90.53; H, 5.45.
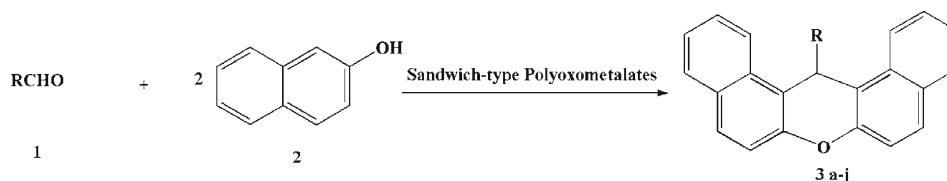
2.7e 14-(4-Methoxyphenyl)-14H-dibenzo[a.j]xanthenes (3g): White solid. m.p.: 202–204°C, IR (KBr): $\overline{v}$ = 3071, 2923, 1735, 1591, 1509, 1458, 1430, 1398, 1248, 1030, 960, 830, 808, 742 cm^{-1}; ^{1}HNMR (500 MHz, CDCl$_3$): δ = 8.42 (2H, d, J = 8.45 Hz), 7.87 (2H, d, J = 7.95), 7.82 (2H, d, J = 8.9), 7.62 (2H, t, J = 8.2 Hz), 7.52 (2H, d, J = 8.8 Hz), 7.40

(4H, m), 6.71 (2H, d, $J = 8.8$ Hz), 6.5 (1H, s), 3.65 (3H, s); ^{13}CNMR (125 MHz, CDCl$_3$): $\delta = 158.2$, 149.1, 137.7, 131.8, 131.5, 129.5, 129.2, 129.1, 127.1, 124.6, 123.1, 118.4, 117.9, 114.2, 55.4, 37.5 ppm; MS (70 eV): $m/z = 388$ (M$^+$, 17.6), 281 (100), 252 (14.1), 57(6); Anal. Calcd. for C$_{28}$H$_{20}$O$_2$: C, 86.59; H, 5.15, Found: C, 86.43; H, 5.24.

2.7f 14-Ethyl-14H-dibenzo[a, j]xanthene (3j): White solid, m.p.: 151–152°C, IR (KBr): $\overline{\nu} = 3064$, 2927, 2873, 1620, 1590, 1514, 1456, 1433, 1399, 1256, 1139, 1029, 958, 829, 750 cm^{-1}; ^{1}HNMR (500 MHz, CDCl$_3$): $\delta = 8.27$ (2H, d, $J = 8.5$ Hz), 7.89 (2H, d, $J = 7.7$ Hz), 7.79 (2H, d, $J = 8.8$ Hz), 7.66–7.45 (4H, m), 7.40 (2H, d, $J = 8.8$ Hz), 5.58 (1H, t, $J = 4.6$ Hz), 2.15–2.03 (2H, m), 0.98 (3H, t, $J = 7.4$ Hz); ^{13}CNMR (125 MHz, CDCl$_3$): $\delta = 150.1$, 131.4, 131, 128.8, 128.2, 126.5, 124, 122.4, 117.5, 115.9, 31.6, 28.3, 9.01 ppm; MS (70 eV): $m/z = 310$ (M$^+$, 5), 281 (100), 252 (30), 140 (25), 57 (65); Anal. Calcd. for C$_{23}$H$_{18}$O: C, 89.03; H, 5.80, Found: C, 89.59; H, 5.97.

3. Results and discussion

In order to optimize the reaction conditions and evaluate the catalytic efficiency of two novel sandwich-type polyoxometalate catalysts, initially a model was chosen on condensation reaction between 4-fluorobenzaldehyde (1 mmol) and β-naphthol (2 mmol) in the presence of different amount of catalysts K$_{12}$[As$_2$W$_{18}$Cu$_3$O$_{68}$]·30H$_2$O and K$_{12}$[As$_2$W$_{18}$U$_3$O$_{74}$]· 21H$_2$O separately under solvent and solvent-free conditions using both conventional heating and microwave irradiation. Results showed that among the tested solvents such as methanol, 1,2-dichloroethane, water, dimethyl formamide and solvent-free system, condensation of 4-fluorobenzaldehyde and β-naphthol was more facile and proceeded to gave highest yield when 1.3 mol% of K$_{12}$[As$_2$W$_{18}$Cu$_3$O$_{68}$]·30H$_2$O and 0.8 mol% of K$_{12}$[As$_2$W$_{18}$U$_3$O$_{74}$]·21H$_2$O under solvent-free conditions are used (table 1). In the absence of catalysts, this reaction could be carried out but the product was obtained in very low yield even after prolonged time. In solvent-free media using microwave

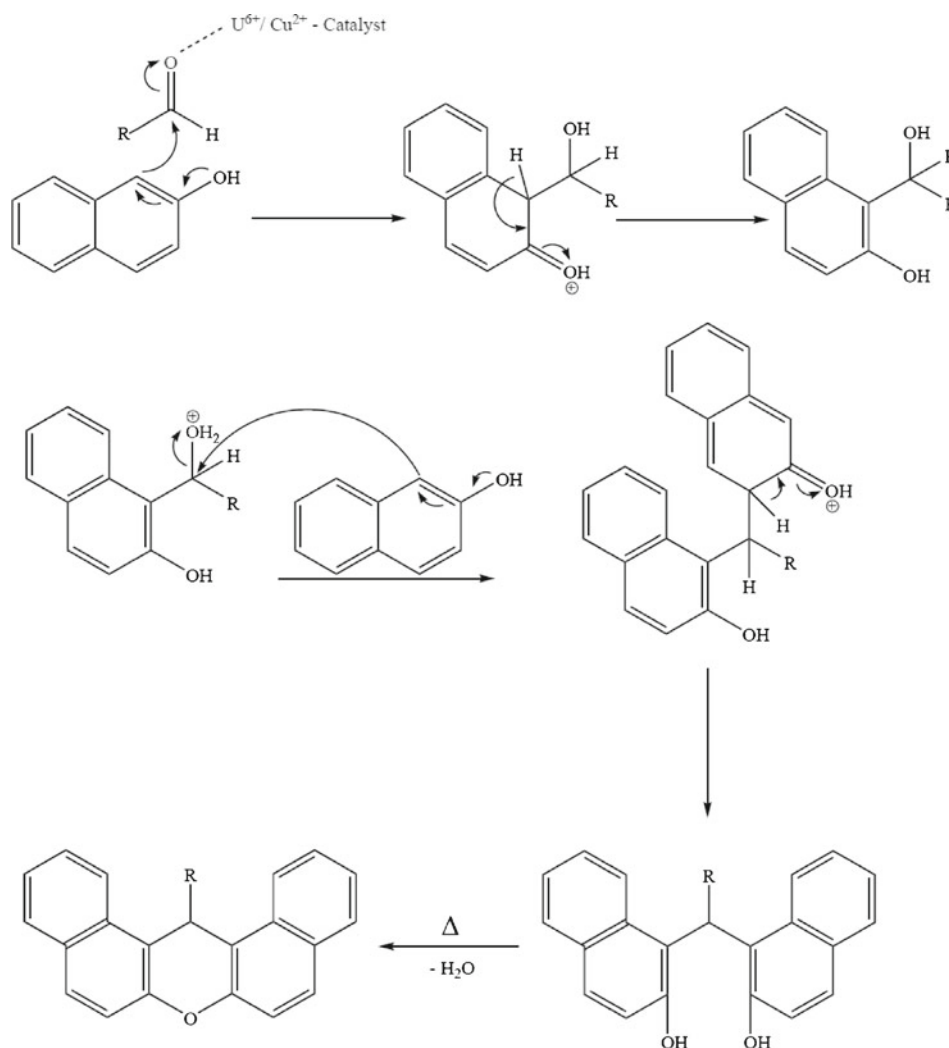**Scheme 1.** Synthesis of 14-aryl or alkyl-14H-dibenzo[a, j]xanthenes in the presence of sandwich-type polyoxometalates.

Table 2. Synthesis of 14-aryl or alkyl-14H-dibenzo[a, j]xanthenes using K$_{12}$[As$_2$W$_{18}$Cu$_3$O$_{68}$]·30H$_2$O (I) and K$_{12}$[As$_2$W$_{18}$U$_3$O$_{74}$]·21H$_2$O (II) catalysts under solvent-free conditions.

| | | | I Method A | I Method B | II Method A | II Method B | |
| | | | Time (h)/ | Time (min)/ | Time (h)/ | Time (min)/ | m.p. (°C) |
Entry	R	Product	Yield (%)^a	Yield (%)^a	Yield (%)^a	Yield (%)^a	Ref.
1	C$_6$H$_5$	**3a**	3.30/89	18.00/89	2.30/88	10.00/85	183–185[43]
2	4-NO$_2$C$_6$H$_5$	**3b**	2.00/93	16.00/91	2.00/91	10.00/95	311–312[44]
3	4-FC$_6$H$_5$	**3c**	2.30/95	15.30/90	2.00/94	8.00/93	239–240[44]
4	4-ClC$_6$H$_5$	**3d**	2.30/91	18.00/87	2.00/92	8.00/90	289–290[44]
5	4-BrC$_6$H$_5$	**3e**	2.30/91	18.00/89	2.30/90	8.30/92	297–299[44]
6	4-CH$_3$C$_6$H$_5$	**3f**	4.00/90	21.30/91	3.00/92	9.00/93	227–229[44]
7	4-OCH$_3$C$_6$H$_5$	**3g**	4.00/88	21.00/85	3.30/89	12.00/85	202–204[44]
8	4-OHC$_6$H$_5$	**3h**	4.30/81	23.00 /81	4.00/82	12.00/79	140[45]
9	CH$_3$	**3i**	4.00/76	25.00/74	3.30/75	12.00/72	149
10	CH$_3$CH$_2$	**3j**	4.00/78	24.00/79	4.00/80	12.00/77	151–152[44]

Method A: reaction carried out under conventional heating in solvent-free conditions
Method B: reaction carried out under microwave irradiation in solvent-free conditions
^{a}Yields refer to pure products and all products were characterized from their spectral data and were compared with authentic samples

Scheme 2. Proposed mechanism for the synthesis of 14-substituted-14H-dibenzo[a, j]xanthenes.

irradiation $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ catalyst facilitated the formation of dibenzo[a, j]xanthene in good yield, but $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ catalyst requires long reaction time. It was found that under solvent-free conditions, the catalytic activities of $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ and $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot$

Table 3. Synthesis of 14-(4-fluorophenyl)-14H-dibenzo[a, j]xanthenes using different catalysts.

Catalyst	Conditions	Yield (%)	Time (h)	Ref.
$K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$	Solvent-free/125°C	95	2.30	This work
$K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$	Microwave irradiation	90	15.30 min	This work
$K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$	Solvent-free/125°C	94	2.00	This work
$K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$	Microwave irradiation	93	8.00 min	This work
$H_6[P_2W_{18}O_{62}]\cdot24H_2O$	Solvent-free/100°C	90	1.00	[39]
$H_3[PW_{12}O_{40}]\cdot3H_2O$	Solvent-free/100°C	85	1.00	[39]
$K_5[CoW_{12}O_{40}]\cdot3H_2O$	Solvent-free/125°C	94	2.00	[43]
Indion-130	Solvent-free/110°C	92	18.00 min	[41]
$HClO_4$-SiO_2	1,2 – Dichloroethane (reflux)	94	9.00	[34]
$KAl(SO_4)_2\cdot12H_2O$	Water (reflux)	91	4.00	[37]
P_2O_5	Solvent-free/80°C	91	50.00 min	[40]
$InCl_3$	Solvent-free/80°C	82	65.00 min	[40]
$Yb(OTf)_3$	Solvent-free/90°C	93	1.00	[36]

$30H_2O$ were increased. In all the cases, $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ was found to be a better catalyst than $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ (table 1).

After optimization of the reaction conditions, the generality of these conditions to other substrates was studied. Various substituted aromatic and aliphatic aldehyde were selected to undergo the reaction with β-naphthol in the presence of $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ and $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ catalysts to produce the corresponding 14-aryl or alkyl-14H-dibenzo[a, j]xanthenes under solvent-free conditions (scheme 1). The results are summarized in table 2.

It was indicated that, electronic effects and the nature of the substituted functional groups on the aldehyde were affected on the reaction time. In comparison with electron with-drawing groups on the aryl aldehydes (table 2, entries 2–5), it was found that the presence of electron donating groups on the aromatic ring (table 2, entries 6–8) and also aliphatic aldehydes decreased reaction rate (table 2, entries 9 and 10) and needed a longer reaction time to give satisfactory yield.

In a typical experimental procedure, when reaction was complete, the catalyst was filtered, washed with ethyl acetate, dried at 70°C for 1 h, and finally reloading the same catalyst for the new run without any appreciable loss of activity.

Role of metal salts as Lewis acid catalysts in carbon–carbon bond formation and other organic transformations is well-established.[46] The probable mechanism for the formation of dibenzo xanthenes is expected to proceed via initial condensation of aldehyde with β-naphthol to afford the intermediate (phenyl- or alkyl-methylenebisnaphthols), which underwent dehydration to give the final product, in the presence of sandwich type polyoxometalates. The carbonyl group of aldehyde was activated through coordination to U^{6+} or Cu^{2+} in $[As_2W_{18}U_3O_{74}]^{12-}$ and $[As_2W_{18}Cu_3O_{68}]^{12-}$, so that electrophilic property of benzaldehyde increase, also polyoxometalates can stabilize organic intermediates. According to suggested mechanism in the article text for this reaction,[33,47,48] we propose that aryl- or alkyl-methylenebisnaphthols are formed in the fast steps, which then undergo dehydration-cyclization in the slow step to give the final product which correlate with the nature of the substituents (scheme 2).

The most intense peak in all compounds were appeared at m/z = 281, corresponds to the loss of aryl or alkyl groups in synthesized 14-aryl or alkyl-14H-dibenzo[a, j]xanthenes. In addition, the absence of OH resonance in the ^1H NMR and OH vibrations in the IR confirms the structure of our products. In all the ^1H NMR spectra, the characteristic peak of 14-H xanthene was appeared in 5.5–6.6 ppm region as a singlet.

Table 3 compares efficiency of $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ and $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ (time, yield, reaction conditions) with efficiency of other catalysts in synthesis of 14-(4-fluorophenyl)-14H-dibenzo[a, j]xanthene obtained by other groups. As it can be seen, the used method is simpler, more efficient, and without toxic solvents.

4. Conclusions

In this work, we have developed a facile and efficient method using sandwich-type polyoxometalates, $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ and $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$, as catalysts for one-pot synthesis of 14-substituted-14H-dibenzo[a, j]xanthenes from β-naphthol and various aldehydes. The catalytic activity of these catalysts is remarkable and these are environmentally benign. The advantages such as solvent-free reaction conditions, shorter reaction time, simplicity of the reaction, high product yields and the recycling of the catalyst make $K_{12}[As_2W_{18}U_3O_{74}]\cdot21H_2O$ and $K_{12}[As_2W_{18}Cu_3O_{68}]\cdot30H_2O$ as an efficient catalysts.

References

1. Pope M T 1983 *Heteropoly and isopoly oxometalates* (Berlin: Springer)
2. Pope M T and Muller A 1994 *Polyoxometalates: From platonic solids to anti-retroviral activity* (Dordrecht, Netherlands: Kluwer)
3. Hill C L 1998 *Chem. Rev.* **98** 1
4. Clemente-Juan J M and Coronado E 1999 *Coord. Chem. Rev.* **361** 193
5. Pope M T and Muller A 2001 *Polyoxometalate chemistry: From topology via self- assembly to applications* (Dordrecht, Netherlands: Kluwer)
6. Wu S, Zhang W, Wang J and Ren X 2008 *Catal. Lett.* **123** 276
7. Wang X L, Qin C, Wang E B, Su Z M, Li Y G and Xu L 2006 *Angew. Chem. Int. Ed.* **45** 1
8. Lu Y, Xu Y, Li Y G, Wang E B, Xu X X and Ma Y 2006 *Inorg. Chem.* **5** 2055
9. An H Y, Li Y G, Xiao D R, Wang E B and Sun C Y 2006 *Cryst. Growth Des.* **5** 1107
10. Wu C D, Lu C Z, Zhuang H H and Huang J S 2002 *J. Am. Chem. Soc.* **124** 3836
11. Hagrman P J, Hagrman D and Zubieta J 1999 *Angew. Chem. Int. Ed.* **38** 3165
12. Zheng S T, Yuan D Q, Zhang J and Yang G Y 2007 *Inorg. Chem.* **46** 4569
13. Drewes D, Limanski E M and Krebs B 2005 *Eur. J. Inorg. Chem.* **44** 1542
14. Mbomekalle I M, Keita B, Nieerlich M, Kortz U, Berthet P and Nadjo L 2003 *Inorg. Chem.* **42** 5143
15. Witte P T, Chowdhury S R, Elshof J E, Sloboda-Rozner D and Alsters R N P L 2005 *Chem. Commun.* 1206

16. Santos I C M S, Gamelas J A F, Balula M S S, Simões M M Q, Neves M G P M S, Cavaleiro J A S and Cavaleiro A M V 2007 *J. Mol. Catal. A: Chem.* **262** 41
17. Egusquiza M G, Romanelli G P, Cabello C I, Botto I L and Thomas H J 2008 *Catal. Commun.* **9** 45
18. Hideo T 1981 *Chem. Abstr.* **95** 80922b
19. Lambert R W, Martin J A, Merrett J H, Parkes K E B and Thomas G J 1997 *Chem. Abstr.* **126** 212377y
20. Ion R M 1997 *Prog. Catal.* **2** 55
21. Ion R M, Frackowiak D, Planner A and Wiktorowicz K 1998 *Acta Biochim. Pol.* **45** 833
22. Banerjee A and Mukherjee A K 1981 *Stain Technol.* **56** 83
23. Ahmad M, King T A, Ko D K, Cha B H and Lee J 2002 *J. Phys. D. Appl. Phys.* **35** 1473
24. Knight C G and Stephens T 1989 *Biochem. J.* **258** 683
25. Wolf W 1893 *Chem. Ber.* **26** 83
26. Rosebush I K 1955 *Das. Leder.* **6** 58
27. Papini P and Cimmarusti R 1947 *Gazz. Chim. Ital.* **77** 142
28. Ota K and Kito T 1976 *Bull. Chem. Soc. Jpn.* **49** 1167
29. Khorramabadi-zad A, Kazemi Z and Amini Rudbari H 2002 *J. Korean Chem. Soc.* **46** 541
30. Sarma R J and Baruah J B 2005 *Dyes Pigm.* **64** 91
31. Khorramabadi-Zad A, Akbari S A, Shiri A and Veisi H 2005 *J. Chem. Res.* 277
32. Rajitha B, Kumar B S, Reddy Y T, Reddy P N and Sreenivasulu N 2005 *Tetrahedron Lett.* **46** 8691
33. Ko S and Yao C F 2006 *Tetrahedron Lett.* **47** 8827
34. Bigdeli M A, Heravi M M and Mahdavinia G H 2007 *J. Mol. Catal. A* **275** 25
35. Shakibaei G I, Mirzaei P and Bazgir A 2007 *Appl. Catal A* **325** 188
36. Su W, Yang D, Jin C and Zhang B 2008 *Tetrahedron Lett.* **49** 3391
37. Dabiri M, Baghbanzadeh M, Shakourinikcheh M and Arzroomchilar E 2008 *Bioorg. Med. Chem. Lett.* **18** 436
38. Sharifi A, Abaee S, Tavakoli A, Mirzaei M and Zolfagharei A 2008 *Synth. Commun.* **38** 2965
39. Amini M M, Seyyedhamzeh M and Bazgir A 2007 *Appl. Catal. A Gen.* **323** 242
40. Karimi-Jaberi Z and Hashemi M M 2008 *Monatsh. Chem.* **139** 605
41. Kantevari S, Chary M V, Das A P R, Vuppalapati S V N and Lingaiah N 2008 *Catal. Commun.* **9** 1575
42. Khoshnavazi R, Eshtiagh-Hosseini H, Alizadeh M H and Pope M T 2007 *Inorg. Chim. Acta* **360** 686
43. Nagarapu L, Kantevari S, Mahankhali V C and Apuri S 2007 *Catal. Commun.* **8** 117
44. Khosropour A R, Khodaei M M and Moghannian H 2005 *Synlett.* 955
45. Kumar P S, Kumar B S, Rajitha B, Reddy P N, Sreenivasula N and Reddy Y T 2006 *Arkivoc* **xii** 46
46. (a) Schinzer D (ed.) 1989 *Selectivities in lewis acid promoted reactions* (Dordrecht: Kluwer Academic Publishers); (b) Yamamoto H (ed.) 2000 *Lewis acids in organic synthesis* (Weinheim: Wiley-VCH); (c) Hay R W, Wilkinson G, Gillard R D and McCleverty J A 1987 *Comprehensive coordination chemistry* (Oxford: Pergamon Press) p. 411; (d) Santelli M 1995 *Lewis acids and selectivity in organic synthesis*, Boca Raton: CRC Press; (e) Wang L M, Sui Y and Zhang L 2008 *Chin. J. Chem.* **26** 1105
47. Ding F Q, An L T and Zou J P 2007 *Chin J. Chem.* **25** 645
48. (a) Wang L M, Xia J J, Qin F, Qian C T and Sun J 2003 *Synthesis* **8** 1241; (b) Wang L M, Sheng J, Tian H and Qian C T 2004 *Synth. Commun.* **34** 4265; (c) Wang L M, Liu J J, Tian H, Qian C T and Sun J 2005 *J. Adv. Synth. Catal.* **347** 689; (d) Wang L M, Sheng J, Zhang L, Han J W, Fan Z Y and Tian H 2005 *Tetrahedron* **61** 1539