Supporting file

Cesium salt of 2-molybdo-10-tungstophosphoric acid as an efficient and reusable catalyst for the synthesis of uracil derivatives via green route

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1.Experimental section

1.1. Materials and methods

Disodium phosphate (Na\textsubscript{2}HPO\textsubscript{4}), sodium molybdate (Na\textsubscript{2}MoO\textsubscript{4}.2H\textsubscript{2}O), sodium tungstate (Na\textsubscript{2}WO\textsubscript{4}.2H\textsubscript{2}O), and cesium carbonate (Cs\textsubscript{2}CO\textsubscript{3}) were purchased from Molychem in India and used without further purification. The other additional chemicals and solvents used in the organic synthesis purchased from Alfa Aesar, Sigma Aldrich, and Merck.

The functional integrity and primary Keggin structure of the modified heteropoly anions and after a partial exchange of the protons by cesium cations investigated by FT-IR (Bruker ALPHA Eco-ATR). The elemental composition of catalysts for the derived molecular formula investigated by EDX (FEI Nova Nano SEM 450 combined Bruker XFlash 6I30) element image mapping and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, PerkinElmer Inc.). The specific surface area and pore volume determined by nitrogen gas adsorption-desorption at 77.35 K using the BET method (NOVA Quanta chrome instruments version 11.05). XRD technique used to define the crystallinity and secondary Keggin structure. The SEM-TEM analysis was used to study the microtopography.

In organic synthesis, the reaction progress was monitored by using thin-layer chromatography (Merck's silica plates) and imagining accomplished by ultraviolet light or iodine. Melting points of all the synthesized analogs set in the open capillary tube. However, \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded to confirm the obtained product structure (Bruker Avance 400 Spectrometer).
1.2. Preparation of 2-molybdo-10-tungstophosphoric acid ($\text{H}_3\text{[PW}_{10}\text{Mo}_2\text{O}_{40}]$):

The precursor for catalyst preparation was synthesized by the simple procedure as follows. Firstly, the desired amount of disodium phosphate (20.66 mmol) and sodium tungstate (206.64 mmol) dissolved in deionized distilled water (25ml). The obtained solution stirred for 30 minutes at 90°C. Then the necessitated amount of aqueous sodium molybdate (41.33 mmol) was added to the above-heated solution. Subsequently, the addition of aqueous sulphuric acid (537.26 mmol) was done until the pH of the solution reached roughly in the range of 1.5 to 2. The resulting mixture was kept in the autoclave at 90°C for 6 hours. Finally, the reaction mixture was cooled and extracted with diethyl ether to get the etherate solution. The 2-molybdo-10-tungstophosphoric acids crystals were obtained by the recrystallization of concentrated etherate solution in deionized distilled water.

1.3. Preparation of cesium salts of 2-molybdo-10-tungstophosphoric acid as a catalyst:

The synthesis of catalyst was done by a simple titration method. Characteristically, a stoichiometric amount of Cs$_2$CO$_3$ was added to the aqueous solution of 2-molybdo-10-tungstophosphoric acids (3.7mmol) at a constant rate. The Cs content, $x$ in Cs$_x$H$_3$.$x$PW$_{10}$Mo$_2$O$_{40}$, was adjusted by the amount 1.85, 3.70, and 4.50 mmol of Cs$_2$CO$_3$ for Cs-1, Cs-2, and Cs-3 respectively in solution. After complete addition, the procedure was done with continuous stirring and heating the resultant solution for 120 minutes at 60°C. Then, the water evaporated by heating, and the solid was dried in an oven at 100°C, giving the cesium salt of heteropoly acid, denoted as Cs-1, Cs-2, and Cs-3.

1.4. General procedure for the synthesis of pyrimido[4,5-b]quinolines(4a-4j):

A mixture of compounds consisting of aldehyde (1 mmol), dimedone (0.140 g, 1 mmol), 6-amino-1,3-dimethyluracil (0.155 g, 1 mmol) and Cs$_{2.3}$H$_{0.7}$PW$_{10}$Mo$_2$O$_{40}$ (0.003 g) was stirred vigorously at 70 °C then the progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture cooled at room temperature, EtOAc (20 mL) was added, and boiled for 5 min, then centrifuged and decanted to separate the insoluble catalyst. The solvent of the solution obtained from the decanting evaporated, and then the crude product was recrystallized from ethanol to give the pure product.

1.5. Recyclation procedure of catalyst:
For studying reusability of catalyst, after completion of reaction the catalyst was recovered from reaction mixture by simple filtration method. The recovered catalyst was washed with ethanol/water system (1:1) and dried in oven for 60 min at 110 °C temperature then reused in a next run.

2. Figures

Figure 1. FT-IR spectra of (a) H$_3$PW$_{10}$Mo$_2$, (b) Cs-1, (c) Cs-2, (d) Cs-3, and (d$_r$) recovered Cs-3 after nine cycles

Figure 2. XRD pattern of (a) H$_3$PW$_{10}$Mo$_2$, (b) Cs-1, (c) Cs-2, (d) Cs-3, and (d$_r$) recovered Cs-3 after nine cycles
Figure 3. EDX spectra of (a) H₃PW₁₀Mo₂, (b) Cs-1, (c) Cs-2, and (d) Cs-3
Figure 4. Nitrogen adsorption–desorption isotherms of (a) H$_3$PW$_{10}$Mo$_2$, (b) Cs-1, (c) Cs-2, and (d) Cs-3
Figure 5. SEM-TEM images of (a) H$_3$PW$_{10}$Mo$_2$, (b) Cs-1, (c) Cs-2, and (d) Cs-3

Spectral Data

1,3,8,8-tetramethyl-5-phenyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,7H)-trione (4a)

MS 365 (M$^+$), IR (KBr) 3015, 2962, 1712, 1652, 1558, 1541, 1508, 1482 cm$^{-1}$

H NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 0.89 (s, 3H), 1.05 (s, 3H), 2.05 (d, $J = 16.0$ Hz, 1H), 2.23 (d, $J =
16.1 Hz, 1H), 2.52-2.65 (distorted AB system, 2H), 3.10 (s, 3H), 3.47 (s, 3H), 4.89 (s, 1H), 7.09 (t, $J = 7.1$ Hz, 1H, HAr), 7.17-7.25 (m, 4H), 9.02 (s, 1H). $^{13}$C NMR 204.4, 160.3, 159.6, 151.2, 150.4, 149.5, 139.7, 132.4, 130.2, 127.4, 120.9, 105.5, 31.7, 29.9, 28.3, 23.5.

5-(4-chlorophenyl)-1,3,8,8-tetramethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,7H)-trione (4b)

MS 399 (M$^+$), IR (KBr) 3005, 2948, 1709, 1660, 1588, 1548, 1512, 1480 cm$^{-1}$. $^1$H NMR (250 MHz, DMSO-d$_6$): $\delta$ (ppm) 0.85 (s, 3H), 1.00 (s, 3H), 2.01 (d, $J = 16.1$ Hz, 1H), 2.19 (d, $J = 16.1$ Hz, 1H), 2.47-2.55 (distorted AB system, 2H), 3.06 (s, 3H), 3.42 (s, 3H), 4.83 (s, 1H), 7.14-7.28 (m, 5H). $^{13}$C NMR 204.5, 160.5, 159.7, 151.2, 151.4, 150.2, 148.2, 143.4, 129.7, 122.2, 121.5, 105.5, 31.6, 29.9, 28.3, 23.5.

5-(4-bromophenyl)-1,3,8,8-tetramethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,7H)-trione (4c)

MS 443 (M$^+$), IR (KBr) 3025, 2965, 1712, 1675, 1558, 1536, 1513, 1470 cm$^{-1}$. $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ (ppm) 0.90 (s, 3H), 1.03 (s, 3H), 2.03-2.10 (distorted AB system, 2H), 2.20-2.28 (distorted AB system, 2H), 3.09 (s, 3H), 3.45 (s, 3H), 4.85 (s, 1H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 9.04 (s, 1H). $^{13}$C NMR 204.4, 160.3, 159.6, 151.2, 150.4, 149.5, 139.7, 132.4, 130.2, 127.4, 120.9, 105.5, 31.7, 29.9, 28.3, 23.5.

(5-(4-(dimethylamino)phenyl)-1,3,8,8-tetramethyl-7,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,5H)-trione) (4d)

MS 408 (M$^+$), IR (KBr) 3020, 2960, 1717, 1670, 1555, 1532, 1512, 1472 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 7.00 (d, $J = 8.7$ Hz, 7H), 6.52 (d, $J = 8.8$ Hz, 7H), 4.72 (s, 3H), 3.41 (s, 10H), 3.07 (s, 10H), 2.77 (s, 18H), 2.20 (d, $J = 16.2$ Hz, 4H), 2.01 (d, $J = 16.3$ Hz, 5H), 1.02 (s, 9H), 0.89 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta = 195.69, 161.53, 151.07, 149.34, 135.03, 128.74, 112.57, 91.41, 50.61, 40.72, 32.93, 32.48, 30.52, 29.51, 28.12, 26.89.

1,3,8,8-tetramethyl-5-(3-nitrophenyl)-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,5H)-trione (4e)

MS 410 (M$^+$), IR (KBr) 3017, 2960, 1713, 1655, 1560, 1540, 1508, 1482 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 0.91 (s, 3H), 1.06 (s, 3H), 2.06 (d, $J = 16.2$ Hz, 1H), 2.26 (d, $J = 16.4$ Hz, 1H), 2.57-2.69 (distorted AB system, 2H), 3.09 (s, 3H), 3.47 (s, 3H), 4.98 (s, 1H), 5.01-5.06 (distorted AB system, 2H), 7.01 (t, $J = 7.8$ Hz, 1H, HAr), 7.19-7.25 (m, 4H), 9.05 (s, 1H). $^{13}$C NMR 204.4, 160.3, 159.6, 151.2, 150.4, 149.5, 139.7, 132.4, 130.2, 127.4, 120.9, 105.5, 31.7, 29.9, 28.3, 23.5.
7.52 (m, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.98 (dd, J = 8.2, 1.4 Hz, 1H), 8.05 (s, 1H), 9.18 (s, 1H); 13C NMR 199.5, 161.5, 158.5, 150.8, 142.0, 141.8, 137.1, 128.8, 128.4, 113.9, 91.5, 55.1, 37.4, 29.8, 28.7, 28.2, 19.8.

5-(4-hydroxyphenyl)-1,3,8,8-tetramethyl-7,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,5H)-trione (4f)

MS 381 (M^+), IR (KBr) 3020, 2950, 1726, 1660, 1552, 1523, 1522, 1460 cm\(^{-1}\).¹H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) (ppm) 6.98 (d, J = 8.5 Hz, 2H), 6.54 (d, J = 8.5 Hz, 2H), 4.73 (s, 1H), 3.40 (s, 3H), 3.06 (s, 3H), 2.52 (s, 2H), 2.18 (d, J = 16.1 Hz, 1H), 2.00 (d, J = 16.4 Hz, 1H), 1.00 (s, 3H), 0.85 (s, 3H). 13C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) = 195.64, 161.31, 155.57, 151.05, 149.83, 143.97, 137.56, 128.96, 114.82, 112.46, 91.11, 70.15, 50.48, 40.19, 39.52, 33.16, 32.45, 30.52, 29.53, 28.12, 26.72.

5-(2-hydroxy-4-methoxyphenyl)-1,3,8,8-tetramethyl-7,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,5H)-trione (4g)

MS 411 (M^+), IR (KBr) 3020, 2930, 1712, 1662, 1570, 1532, 1525, 1462 cm\(^{-1}\).¹H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) (ppm) 6.66 (t, J = 5.7 Hz, 2H), 6.63 (s, 1H), 6.56 (s, 1H), 4.95 (s, 1H), 3.67 (s, 3H), 3.41 (s, 3H), 3.08 (s, 3H), 2.56 (d, J = 14.2 Hz, 2H), 2.23 (d, J = 16.3 Hz, 1H), 2.03 (d, J = 16.2 Hz, 1H), 1.02 (s, 3H), 0.90 (s, 3H). 13C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) = 196.47, 162.59, 151.61, 150.70, 149.15, 143.17, 134.09, 120.93, 119.88, 111.43, 110.44, 90.26, 70.14, 55.86, 50.23, 40.18, 32.43, 30.72, 29.40, 28.73, 28.36, 26.88.

5-(4-methoxyphenyl)-1,3,8,8-tetramethyl-7,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,5H)-trione (4h)

MS 395 (M^+), IR (KBr) 3020, 2950, 1726, 1660, 1540, 1550, 1502, 1456 cm\(^{-1}\).¹H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) (ppm) 7.10 (d, J = 8.7 Hz, 1H), 6.71 (d, J = 8.7 Hz, 1H), 4.78 (s, 1H), 3.64 (s, 1H), 3.41 (s, 1H), 3.06 (s, 1H), 2.53 (d, J = 5.5 Hz, 1H), 2.10 (d, J = 5.9 Hz, 1H), 1.01 (s, 2H), 0.86 (s, 1H). 13C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) = 195.43, 161.09, 157.64, 150.85, 128.80, 113.32, 112.05, 90.73, 55.13, 50.25, 33.07, 32.26, 30.34, 29.26, 27.91, 26.60.

1,3,8,8-tetramethyl-5-(p-tolyl)-7,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,5H)-trione (4i)
MS 379 (M$^+$), IR (KBr) 3020, 2950, 1722, 1666, 1559, 1510, 1470 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 7.06 (d, 7H), 6.95 (d, 7H), 4.78 (s, 3H), 3.41 (s, 9H), 3.05 (s, 9H), 2.53 (s, 5H), 2.19 (d, 4H), 2.16 (s, 9H), 2.00 (d, 4H), 1.01 (s, 9H), 0.85 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ = 195.43, 161.09, 157.64, 150.85, 128.80, 113.32, 112.05, 90.73, 55.13, 50.25, 33.07, 32.26, 30.34, 29.26, 27.91, 26.60.

5-(3,4-dimethoxyphenyl)-1,3,8,8-tetramethyl-7,8,9,10-tetrahydropyrimido[4,5-b]
quinoline-2,4,6(1H,3H,5H)-trione (4j)

MS 425 (M$^+$), IR (KBr) 3022, 2970, 1715, 1640, 1556, 1525, 1520, 1460 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 6.81 (s, 1H), 6.70 (dd, $J = 22.3$, 8.2 Hz, 2H), 4.78 (s, 1H), 3.64 (d, $J = 7.5$ Hz, 7H), 3.40 (s, 3H), 3.07 (s, 3H), 2.53 (d, $J = 9.0$ Hz, 2H), 2.20 (d, $J = 16.2$ Hz, 1H), 2.01 (d, $J = 16.2$ Hz, 1H), 1.01 (s, 3H), 0.88 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ = 195.70, 161.37, 151.03, 150.16, 148.38, 147.50, 143.98, 139.41, 119.85, 112.24, 111.71, 90.97, 55.80, 50.44, 33.58, 32.43, 30.53, 29.60, 28.14, 26.67.

The IR Spectrum of Compound (4a)

The $^1$H NMR spectrum of compound (4a)
The $^{13}$C NMR spectrum of compound (4a)

The IR Spectrum of Compound (4b)
The $^1$H NMR spectrum of compound (4b)

The $^{13}$C NMR spectrum of compound (4b)
The IR Spectrum of Compound (4c)

The $^1$H NMR spectrum of compound (4c)
The $^{13}$C NMR spectrum of compound (4c)

The IR Spectrum of Compound (4d)
The $^1$H NMR spectrum of compound (4d)

The $^{13}$C NMR spectrum of compound (4d)
The IR Spectrum of Compound (4e)

The $^1$H NMR spectrum of compound (4e)
The $^{13}$C NMR spectrum of compound (4e)

The IR Spectrum of Compound (4f)
The $^1$H NMR spectrum of compound (4f)

The $^{13}$C NMR spectrum of compound (4f)
The IR Spectrum of Compound (4g)

The $^1$H NMR spectrum of compound (4g)
The $^{13}$C NMR spectrum of compound (4g)

The IR Spectrum of Compound (4h)
The $^1$H NMR spectrum of compound (4h)

The $^{13}$C NMR spectrum of compound (4h)
The IR Spectrum of Compound (4i)

The $^1$H NMR spectrum of compound (4i)
The $^{13}$C NMR spectrum of compound (4i)

The IR Spectrum of Compound (4j)
The $^1$H NMR spectrum of compound (4j)

The $^{13}$C NMR spectrum of compound (4j)

Table S1: ICP-AES data
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Reference