Incorporation of Keggin-Based H$_3$PW$_7$Mo$_5$O$_{40}$ into Bentonite: Synthesis, Characterization and Catalytic Application

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S1. EDS analysis graph:

**Figure 1.** EDS of (a) bulk PW$_7$Mo$_5$ (b) 20% PW$_7$Mo$_5$/Bentonite catalyst.
S2. Elemental mapping images:

Figure 2. Elemental mapping images of (a) bulk PW₇Mo₅ (b) 20% PW₇Mo₅/Bentonite catalyst.

S3. Recovered 20% PW₇Mo₅/Bentonite catalyst.

Figure 3. FT-IR (a) and XRD (b) analysis of recovered 20% PW₇Mo₅/Bentonite catalyst.
S4. Validation of Green metrics for all synthesized compounds (3a-n & 4a-n)

Calculation of green metrics:

Materials used for green metrics calculation:

**Reactant 1:** Benzaldehyde 0.31 gm (Mol. Wt. = 106.12), 4-Chlorobenzaldehyde 0.42 gm (Mol. Wt. = 140.56), 4-Nitrobenzaldehyde 0.45 gm (Mol. Wt. = 151.12), 4-Bromobenzaldehyde 0.55 gm (Mol. Wt. = 185.02), 4-Flurobenzaldehyde 0.37 gm (Mol. Wt. = 124.11), 3-Nitrobenzaldehyde 0.45 gm (Mol. Wt. = 151.12), 4-Anisaldehyde 0.40 gm (Mol. Wt. = 136.15), 4-Methylbenzaldehyde 0.36 (Mol. Wt. = 120.14), 3-Chloro-4-Flurobenzaldehyde 0.47 gm (Mol. Wt. = 158.56), 3-Bromobenzaldehyde 0.55 gm (Mol. Wt. = 185.02), 4-Hydroxybenzaldehyde 0.36 gm (Mol. Wt. = 122.12), 3-Chlorobenzaldehyde 0.42 gm (Mol. Wt. = 140.56), Salicylaldehyde 0.36 gm (Mol. Wt. = 122.12), Furfural 0.28 gm (Mol. Wt. = 96.09), 2-Chlorobenzaldehyde 0.42 gm (Mol. Wt. = 140.56). **Reactant 2:** 5, 5-dimethyl-1, 3-cyclohexanedione 0.84 gm (Mol. Wt. = 140.18). **Reactant 3:** Ammonium acetate 0.23 gm (Mol. Wt. = 77.08).

Analysis of green metrics:

The following listed formulae were used for calculating E-factor, Atom economy (AE), Reaction mass efficiency (RME), Effective mass yield (EMY), and Optimum efficiency (OE). The Calculated data for compounds 3(a-n) and 4(a-n) are presented in Table 1.

Calculation of green chemistry metrics for one representative entry, viz. 3a

## E-factor = Total mass waste (g) / Mass of product

= Total input (g) – Total output (g) / Total output (g)

e.g. For the product 3a; E-factor = (0.31 gm + 0.84 gm) – 0.959 / 0.959 = 0.19

## Atom Economy (AE) (%) = (Molecular wt. of product)/ (Total molecular wt. of reactants) x 100

e.g. For the product 3a; AE = (350.46) / (106.12 + (2 x 140.18 )) x 100 = 90.67 %

##RME (%) = (Mass of isolated product)/ (Total mass of reactant) x 100
e.g. For the product 3a; RME = (0.959) / (0.31 gm + 0.84 gm) x 100 = 83.39

##EMY (%) = (Mass of Product)/(Mass of non-benign reagents) x 100

e.g. For the product 3a; EMY = (0.959) / (0.31 gm + 0.84 gm) x 100 = 83.39 %

##OE (%) = RME/ AE x 100

e.g. For the product 3a; OE = (83.39) / (90.67) x 100 = 91.97 %

Table 1. Green metrics calculation:

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<th>Entry</th>
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<th>E-factor</th>
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<th>Effective Mass Yield (EMY) %</th>
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</table>

Note: Since the catalyst was recovered during the reaction, therefore it’s used amount is not included in the calculations.
S5. Spectral data of the compounds:

*3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3a).*

IR (ATR, $\nu$ cm$^{-1}$): 685, 835, 1035, 1242, 1364, 1581, 1664, 2958. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 1.09 (s, 6H 2x CH$_3$), 1.23 (s, 6H 2x CH$_3$), 2.37 (m, 8H 4x CH$_2$), 5.54 (s, 1H CH), 7.09 (d, J = 8.2 Hz, 2H Ar-H), 7.22 (t, 1H Ar-H), 7.26 (t, J = 8.4 Hz, 2H Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm) = 27.5, 29.8, 31.5, 32.8, 46.5, 47.1, 115.7, 125.9, 126.8, 128.3, 138.1, 189.6, 190.6.

*9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3b).*

IR (ATR, $\nu$ cm$^{-1}$): 649, 863, 1011, 1091, 1155, 1365, 1576, 2955. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 1.15 (s, 6H 2x CH$_3$), 1.27 (s, 6H 2x CH$_3$), 2.57 - 2.27 (m, 8H 4x CH$_2$), 5.53 (s, 1H CH), 7.07 (d, J= 8.5 Hz, Ar-H), 7.25 (d, J= 8.3 Hz, Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm) = 27.4, 29.6, 31.4, 32.4, 46.4, 47.1, 76.7, 77.1, 77.4, 115.3, 128.2, 128.4, 131.6, 136.7, 189.5, 190.6.

*3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3c).*

IR (ATR, $\nu$ cm$^{-1}$): 677, 843, 1114, 1238, 1342, 1506, 1577, 3200. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 1.12 (s, 6H 2x CH$_3$), 1.24 (s, 6H 2x CH$_3$), 2.55 - 2.30 (m, 8H 4x CH$_2$), 5.57 (s, 1H CH), 7.40 (d, J= 8.4 Hz, 2H Ar-H), 8.10 (d, J= 8.7 Hz, 2H Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm) = 27.5, 29.6, 31.5, 33.3, 46.4, 47.0, 76.7, 77.0, 77.3, 114.9, 123.5, 127.6, 146.2, 189.6, 190.9.

*3,3,6,6-tetramethyl-9-(3-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3f).*

IR (ATR, $\nu$ cm$^{-1}$): 652, 801, 1042, 1148, 1351, 1580, 1661, 2954. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 1.12 (s, 6H 2x CH$_3$), 1.27 (s, 6H 2x CH$_3$), 2.48 - 2.36 (m, 8H 4x CH$_2$), 5.54 (s, 1H CH), 7.49 - 7.35 (m, 2H Ar-H), 8.00 (dt, 1H Ar-H), 8.07-8.02 (s, 1H Ar-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm) = 27.4, 28.8, 31.5, 32.9, 46.1, 47.1, 114.9, 121.1, 122.3, 129.2, 133.0, 140.7, 148.5, 189.7, 191.2.

*9-(3-bromophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3j).*
**9-(3-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3l).**

IR (ATR, \( \nu \) cm\(^{-1}\)): 664, 785, 1033, 1244, 1366, 1581, 2952. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta _H \) (ppm) = 1.05 (s, 6H 2x CH\(_3\)), 1.18 (s, 6H 2x CH\(_3\)), 2.53 - 2.25 (m, 8H 4x CH\(_2\)), 5.49 (s, 1H CH), 7.07 (t, \( J = 8.0 \) 1H Ar-H), 7.14 (t, \( J = 8.0 \) Hz, 1H Ar-H), 7.23 (d, \( J = 7.6 \) Hz, 1H Ar-H), 7.33 (s, 1H Ar-H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta C \) (ppm) = 27.4, 29.7, 31.5, 32.7, 47.1, 115.1, 122.6, 125.5, 129.0, 130.2, 140.8, 189.5, 190.7, 207.1.

**3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4a).**

IR (ATR, \( \nu \) cm\(^{-1}\)): 661, 833, 1035, 1154, 1237, 1363, 1582, 1630, 2956, 3286. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta _H \) (ppm) = 1.10 (s, 6H, 2x CH\(_3\)), 1.23 (s, 6H, 2x CH\(_3\)), 2.45-2.34 (m, 8H 4x CH\(_2\)), 5.55 (s, 1H CH), 7.11 (d, \( J = 8.2 \) Hz, 2H Ar-H), 7.19 (d, \( J = 6.9 \) Hz, 2H Ar-H), 7.26 (s, 1H Ar-H), 7.27 (s, 1H -NH). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta C \) (ppm) = 27.5, 29.6, 31.5, 32.7, 46.4, 47.0, 115.1, 125.0, 126.1, 127.2, 129.4, 134.2, 140.5, 189.5, 190.7.

**9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4b).**

IR (ATR, \( \nu \) cm\(^{-1}\)): 766, 836, 1141, 1215, 1487, 1603, 1645, 2955, 3047, 3351. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta _H \) (ppm) = 0.93 (s, 6H, 2x CH\(_3\)), 1.05 (s, 6H, 2x CH\(_3\)), 2.34 - 2.13 (m, 8H 4x CH\(_2\)), 5.02 (s, 1H CH), 7.14 (d, \( J = 8.2 \) Hz, 2 H), 7.28 - 7.24 (m, 2 H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta C \) (ppm) = 27.1, 29.6, 31.5, 32.7, 33.4, 40.8, 50.7, 128.3, 128.4, 129.5, 131.7, 196.2.

**3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4c).**

IR (ATR, \( \nu \) cm\(^{-1}\)): 693, 826, 1134, 1251, 1336, 1443, 1515, 1639, 2914, 3376. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \( \delta _H \) (ppm) = 0.81 (s, 6H 2x CH\(_3\)), 0.97 (s, 6H 2x CH\(_3\)), 1.94 (d, \( J = 6.5 \) Hz, 2H CH\(_2\)), 2.15 (d, \( J = 6.5 \) Hz, 2H CH\(_2\)), 2.31 (m, 4H 2x CH\(_2\)), 4.87 (s, 1H CH), 7.49 - 7.34 (m, 2H Ar-H), 8.13 - 7.92 (m, 2 H Ar-H), 9.44 (s, 1H -NH). \(^13\)C NMR (100 MHz, DMSO-\(d_6\)) \( \delta C \) (ppm) = 27.0, 29.5, 32.7, 34.4, 50.6, 110.9, 123.5, 129.4, 146.0, 150.5, 155.1, 194.9.
3,3,6,6-tetramethyl-9-(3-nitrophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4e).
IR (ATR, $\nu$ cm$^{-1}$): 685, 893, 1135, 1215, 1478, 1642, 2950, 3178. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$ (ppm) = 0.86 (s, 6H 2x CH$_3$), 1.02 (s, 6H 2x CH$_3$), 2.02 (br. s., 2H CH$_2$), 2.19 (br. s., 2H CH$_2$), 2.39 (br. s., 4H 2x CH$_2$), 4.93 (br. s., 1H CH), 7.50 (br. s., 1H Ar-H), 7.63 (br. s., 1H Ar-H), 7.97 (br. s., 2H Ar-H), 9.48 (br. s., 1H -NH). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$ (ppm) = 26.8, 29.5, 32.6, 34.0, 50.5, 111.0, 121.2, 122.5, 129.7, 134.9, 147.8, 149.7, 150.5, 194.9.

9-(3-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4g).
IR (ATR, $\nu$ cm$^{-1}$): 686, 797, 1136, 1213, 1354, 1592, 1636, 2947, 3058, 3171. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$ (ppm) = 0.87 (s, 6H 2x CH$_3$), 1.01 (s, 6H 2x CH$_3$), 2.01 (d, $J = 15.3$ Hz, 2H CH$_2$), 2.18 (d, $J = 15.4$ Hz, 2H CH$_2$), 2.44 - 2.27 (m, 4H 2x CH$_2$), 4.80 (br. s., 1H CH), 7.29 -6.99 (m, 4H Ar-H), 9.37 (s, 1H -NH). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$ (ppm) = 26.9, 29.5, 32.6, 33.5, 50.6, 111.3, 126.0, 126.7, 128.1, 130.0, 132.7, 149.9, 150.2, 194.9.

9-(3-bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4h).
IR (ATR, $\nu$ cm$^{-1}$): 684, 765, 882, 1009, 1136, 1480, 1602, 1636, 2951, 3054, 3263. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$ (ppm) = 0.82 (s, 6H 2x CH$_3$), 0.96 (s, 6H 2x CH$_3$), 1.97 (br. s., 2H CH$_2$), 2.12 (br. s., 2H CH$_2$), 2.40-3.21 (m 4H 2x CH$_2$), 4.73 (br. s., 1H CH), 7.25-7.09 (m, 4H Ar-H), 9.34 (s, 1H -NH). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$ (ppm) =26.9, 29.6, 32.7, 33.6, 50.6, 111.4, 121.5, 127.1, 128.9, 130.5, 150.2, 194.9.
S6. FT-IR, $^1$H & $^{13}$C NMR spectra of the compounds:

3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3a).
9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3b).
3,3,6,6-tetramethyl-9-(4-nitrophenoxy)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3c)
3,3,6,6-tetramethyl-9-((3-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3f)
9-(3-bromophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3j).
9-(3-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3I).
3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4a).
9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4b).
3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4c).
3,3,6,6-tetramethyl-9-(3-nitrophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4e).
9-(3-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4g).
9-(3-bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4h)