Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

# Supporting Information

# A Highly Efficient Palladium(II)/Polyoxometalate Catalyst System for Aerobic Oxidation of Alcohols

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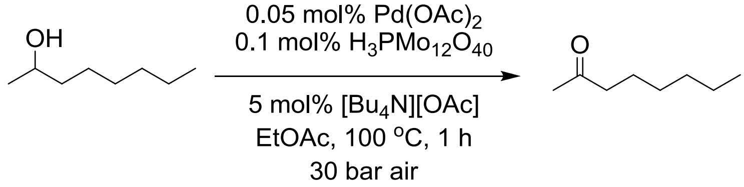
### 1.1 General Considerations

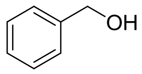
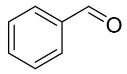
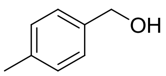
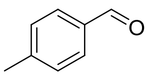
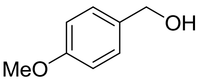
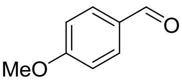
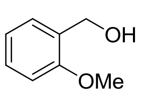
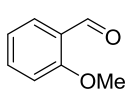
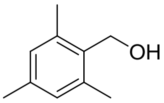
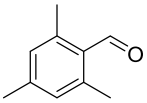
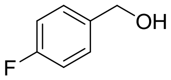
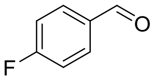
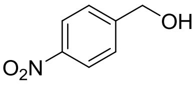
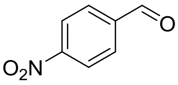
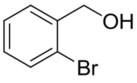
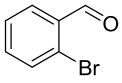
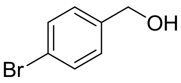
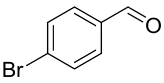
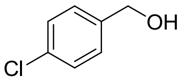
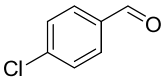
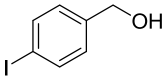
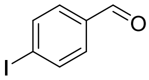
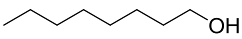
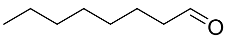
Unless otherwise stated all chemicals were obtained from Sigma Aldrich and used as received. Palladium acetate (99.9 +% trace metals basis). Tetrabutylammonium acetate, ([$Bu_4N$][OAc]) was either 97% grade or 95% grade (Fluorochem) and both gave consistent results after they were dried by heating to 60 °C under high vacuum. $H_3PMo_{12}O_{40}$ was used as received and thermogravimetric analysis indicated 11 number of waters per polyoxometalate. $O_2$:$N_2$ (8:92) and $O_2$:$CO_2$ (8:92) premixed gas cylinders (β standard) and high pressure air cylinder were obtained from BOC gases. $^1$H-NMR spectra were recorded on a Bruker AVX300 (300 MHz) spectrometer at room temperature. Flash column chromatography was performed with 60 Å silica gel as the stationary phase, and all solvents used were of analytical grade. Column chromatography was monitored by thin layer chromatography using Merck silica gel 60 sheets and visualised with UV light or stained with potassium permanganate.

**Caution:** In these studies high pressure $O_2$ gas mixtures (air and 8% $O_2$) and pure $O_2$ atmospheres are employed with organic solvents. Care must be taken during such studies and suitable precautions taken. In the case of reactions using high pressure reactors, we utilise pressures far below the pressure ratings of the vessels and reactors are equipped with safety relief valves. In the case of reactions carried out in glassware with an $O_2$ balloon these are carried out on a small scale (5 mL of solvent) and the reactions are carried out behind a blast shield.

## 1.2 Substrate Scope

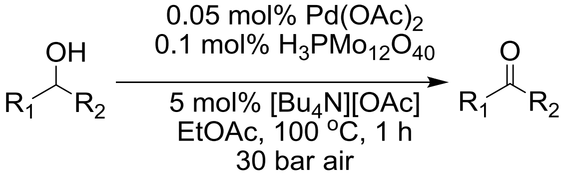
Oxidation of Primary Alcohols:

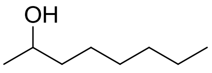
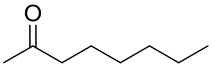
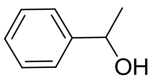
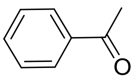
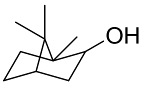
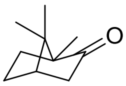
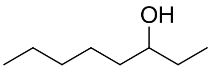
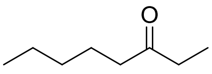
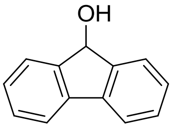
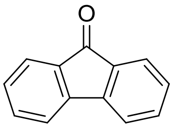
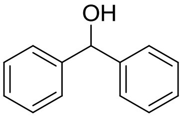
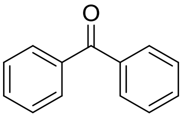
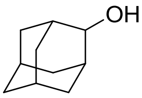
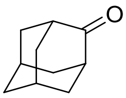
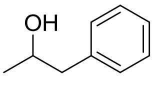
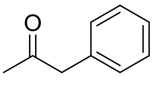
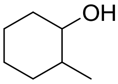
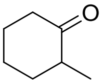
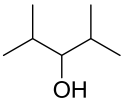
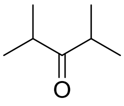
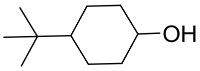
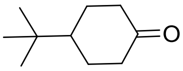
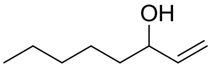
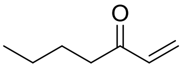


| Entry | Starting Material | | Product | | Conversion[a] | Yield[a] |
|---|---|---|---|---|---|---|
| 1 |  | **1a** |  | **2a** | 99<br>91[b] | 99<br>91[b] |
| 2 |  | **1b** |  | **2b** | 98 | 95 |
| 3 |  | **1c** |  | **2c** | 95 | 95<br>92[c] |
| 4 |  | **1d** |  | **2d** | 100<br>100[b] | 100<br>100[b]<br>95[c] |
| 5 |  | **1e** |  | **2e** | 80 | 80 |
| 6 |  | **1f** |  | **2f** | 84 | 84 |
| 7 |  | **1g** |  | **2g** | 13 | 13 |
| 8 |  | **1h** |  | **2h** | 4 | 0 |
| 9 |  | **1i** |  | **2i** | 3 | 3 |
| 10 |  | **1j** |  | **2j** | 69 | 60 |
| 11 |  | **1k** |  | **2k** | 0 | 0 |
| 12 |  | **1l** |  | **2l** | 62<br>64[d] | 38<br>57[d] |

[a] conversion and yield determined by GC using biphenyl as an internal standard from an average of a minimum of two reactions; [b] 60 bar $O_2$:$N_2$ (8:92); [c] isolated yield; [d] 1 mol% TEMPO was added

Oxidation of Secondary Alcohols:



| Entry | Starting Material | | Product | | Conversion[a] | Yield[a] |
|---|---|---|---|---|---|---|
| 1 |  | **1m** |  | **2m** | 90<br>84[b] | 90<br>84[b] |
| 2 |  | **1n** |  | **2n** | 100<br>93[b]<br>79[d] | 100<br>93[b]<br>79[d] |
| 3 |  | **1o** |  | **2o** | 100 | 100 |
| 4 |  | **1p** |  | **2p** | 96 | 96 |
| 5 |  | **1q** |  | **2q** | 89[b]<br>100[d] | 88[b]<br>99[d]<br>93[c] |
| 6 |  | **1r** |  | **2r** | 100 | 100<br>94[c] |
| 7 |  | **1s** |  | **2s** | 100 | 100<br>96[c] |
| 8 |  | **1t** |  | **2t** | 34 | 32 |
| 9 |  | **1u** |  | **2u** | 100 | 100 |
| 10 |  | **1v** |  | **2v** | 69 | 69 |
| 11 |  | **1w** |  | **2w** | 86 | 86 |
| 12 |  | **1x** |  | **2x** | 38 | 34 |

[a] conversion and yield determined by GC using biphenyl as an internal standard from an average of a minimum of two reactions; [b] 60 bar $O_2$:$N_2$ (8:92); [c] isolated yield; [d] 0.01 mol% $Pd(OAc)_2$

### 1.3 Quantification of conversion and product yield by gas chromatography

Analysis of catalytic reactions was carried out by gas chromatography, using an Agilent 6890N series gas chromatograph. Conversion and product yields were determined using biphenyl as an internal standard. Samples were prepared by filtering through a silica plug with diethyl ether. Biphenyl was used as the internal standard (IS) and added prior to the reaction. Calibrations were carried out to obtain the relative response factors (RF) of the products and starting materials compared to the biphenyl internal standard.

Response factors were obtained using the following equation:

$$\mathrm{RF} = \frac{\mathrm{Area}_{\mathrm{internal\ standard}} \times \mathrm{Moles}_{\mathrm{analyte}}}{\mathrm{Area}_{\mathrm{analyte}} \times \mathrm{Moles}_{\mathrm{internal\ standard}}}$$

Moles of remaining substrate and product were calculated using the following equation:

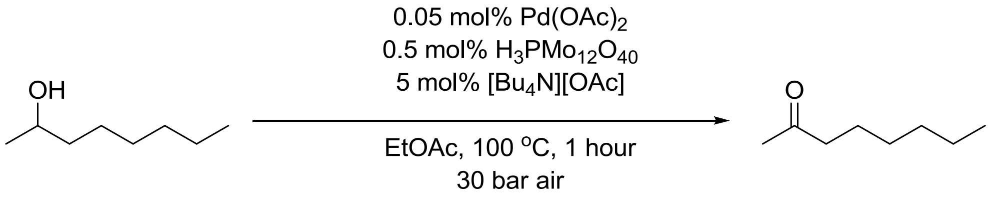
$$\mathrm{Moles}_{\mathrm{analyte}} = \frac{\mathrm{RF} \times \mathrm{Moles}_{\mathrm{internal\ standard}} \times \mathrm{Area}_{\mathrm{analyte}}}{\mathrm{Area}_{\mathrm{internal\ standard}}}$$

Reactions with **1e**, **1i**, **1n**, **1q**, **1r**, **1s**, **1t**, **1w** and **1x** were analysed using a 30 m × 0.32 mm ID SOLGEL-WAX 0.5UM (SGE Analytical Science) column under the following conditions: initial column temperature, 50 °C; initial hold time, 1 min, next temperature, 200 °C; hold time, 0 min; rate of temperature ramp 1, 25 °C/min, final temperature 230 °C; hold time, 18 min; rate of temperature ramp 2, 3 °C/min; injection temperature, 250 °C; detection temperature, 250 °C. The effluent was combusted in an $H_2$/ air flame and detected using a flame ionisation detector (FID).

Reactions with **1a**, **1b**, **1c**, **1d**, **1f**, **1g**, **1h**, **1j**, **1k**, **1l**, **1m**, **1o**, **1p**, **1u** and **1v** were analysed using an Agilent J&W HP-5, (30 m, 0.32 mm, 0.25 µm) silica column, under the following conditions: initial column temperature, 40 °C; initial hold time, 0 min; rate of temperature ramp 1, 4 °C/min; next temperature, 100 °C; hold time, 0 min; rate of temperature ramp 2, 30 °C/min, final temperature 320 °C; hold time, 15 min; injection temperature, 250 °C; detection temperature, 250 °C. The effluent was combusted in a $H_2$/air flame and detected using an FID.

## 2 Additional Optimisation Reactions

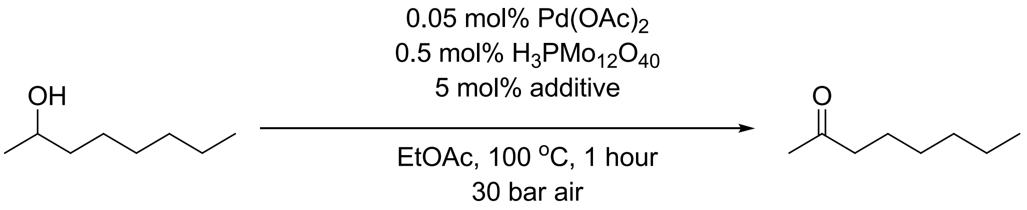
### 2.1 Catalytic component control experiments



| Conditions | % yield |
|---|---|
| No polyoxometalate | 24 |
| No base | 0 |
| No $Pd(OAc)_2$ | 0 |

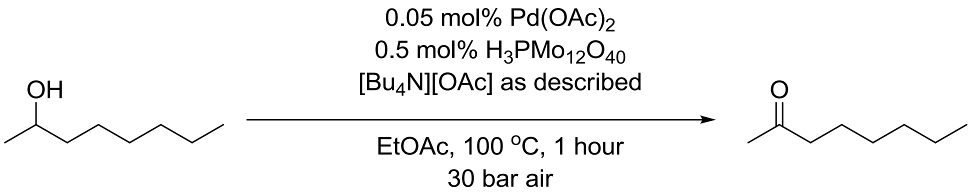
**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g), 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) in 1 mL ethyl acetate under 30 bar pressurized air at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard.

### 2.2 Base Screen



| Base | % Yield |
|---|---|
| $[Bu_4N][OAc]$ | 73 |
| NaOAc | <1 |
| $NaHCO_3$ | <1 |
| 1,8-Diazabicycloundec-7-ene | 0 |
| $[Bu_4N][Br]$ | 0 |
| $[Bu_4N][I]$ | <1 |
| $[Et_4N][Br]$ | <1 |
| $[Et_4N][OAc]$ | 55 |
| $[N_{2228}][NTf_2]$ | 2 |
| $[Bu_4N][OH]$* | 0 |
| Sodium 2-ethylhexanoate | 0 |

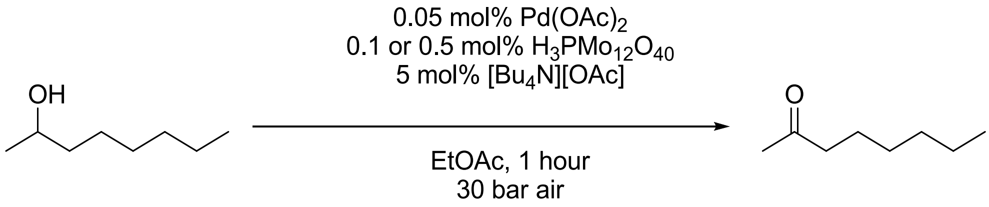
**Conditions:** 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g), 5 mol% base (0.078 mmol) in 1 mL ethyl acetate under 30 bar pressurized air at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard. *$[Bu_4N][OH]$ was added as a 1M aqueous solution.



| Loading of $[Bu_4N][OAc]$ | % yield |
|---|---|
| 0 mol% | 0 |
| 2 mol% | 19 |
| 5 mol% | 73 |
| 10 mol% | 78 |
| 20 mol% | 83 |
| 50 mol% | 79 |

**Conditions:** 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g), $[Bu_4N][OAc]$ as described, in 1 mL ethyl acetate under 30 bar pressurized air at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard.

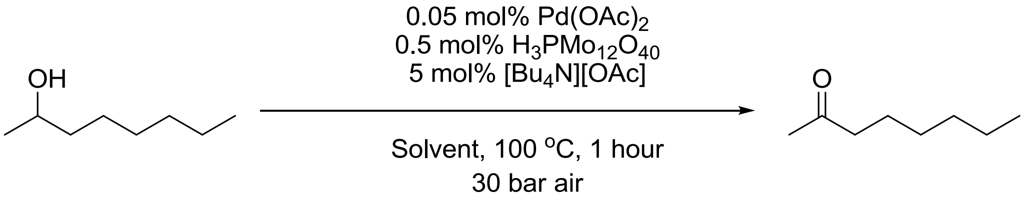
### 2.3 Temperature Screen



| Temperature | 0.5% $H_3PMo_{12}O_{40}$ % Yield | 0.1% $H_3PMo_{12}O_{40}$ % Yield |
|---|---|---|
| 60 °C | 14 | 18 |
| 80 °C | 46 | 57 |
| 100 °C | 73 | 90 |

**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g) or 0.1 mol% $H_3PMo_{12}O_{40}$ (1.56 x$10^{-3}$ mmol, 0.003g), 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) in 1 mL ethyl acetate under 30 bar pressurized air at temperature described for 1 hour. Yield is GC yield in reference to biphenyl internal standard.

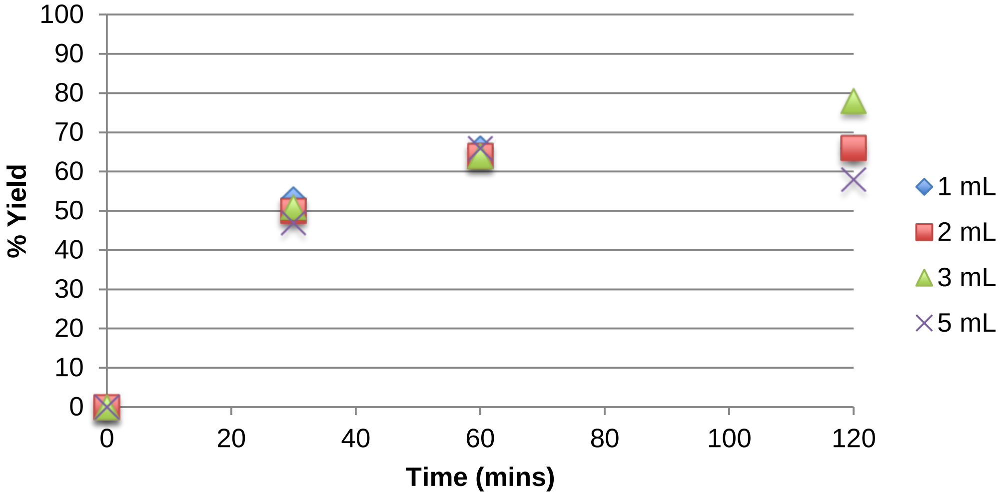
### 2.4 Solvent Screen



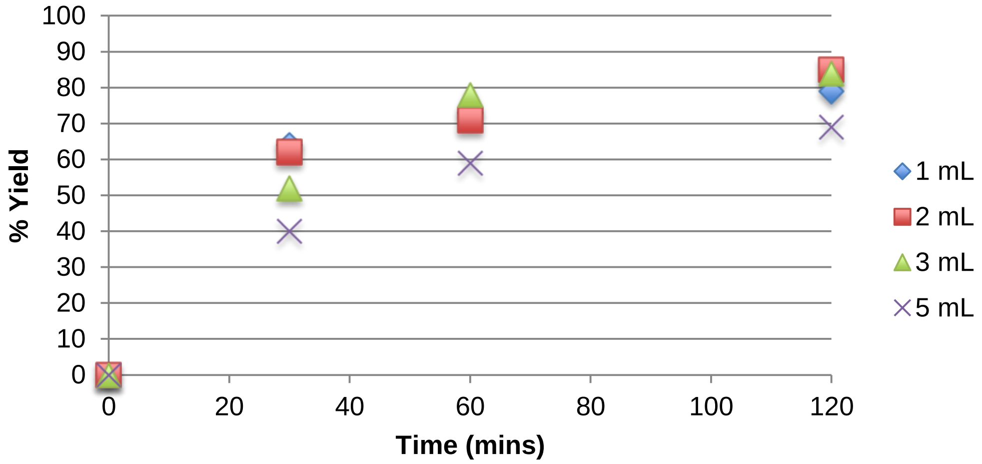
| Solvent | % yield |
|---|---|
| Ethyl Acetate | 73 |
| Toluene | 63 |
| Acetonitrile | 40 |
| DMSO | 26 |
| Tetrahydrofuran | 15 |
| Trifluorotoluene | 90 |
| Dichloromethane | 40 |

**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g), 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) in 1 mL solvent under 30 bar pressurized air at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard.

### 2.5 Effect of reaction concentration



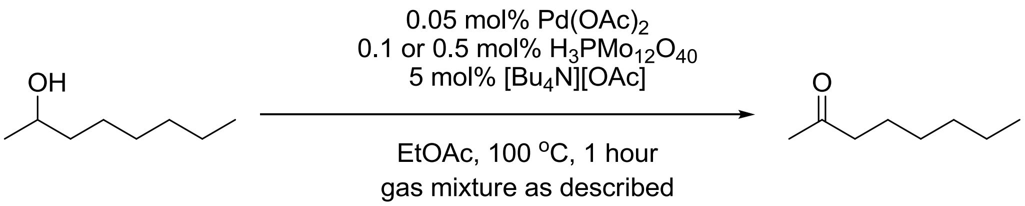
**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g), 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) in 1, 2, 3 or 5 mL EtOAc under 30 bar $O_2$:$N_2$ (8:92) at 100 °C. Yield is GC yield in reference to biphenyl internal standard.



**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g), 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) in 1, 2, 3 or 5 mL EtOAc under 30 bar air at 100 °C. Yield is GC yield in reference to biphenyl internal standard.

In our studies we mostly utilized just 1 mL of solvent; however the graphs above show that more dilute conditions still deliver good reaction rates.

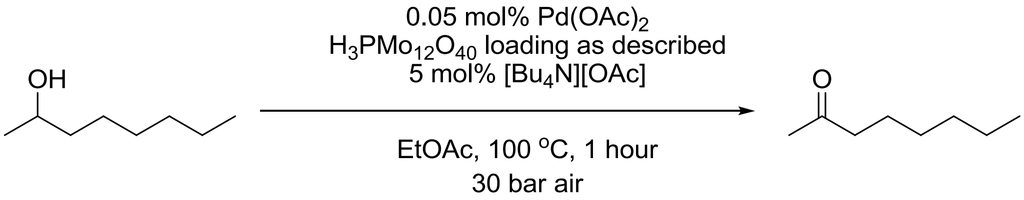
## 2.6 Gas and Pressure Studies



| Gas Composition | Loading of $H_3PMO_{12}O_{40}$ | % yield |
|---|---|---|
| 30 bar air | 0.5 mol% | 73 |
| 30 bar air | 0.1 mol% | 90 |
| 30 bar $O_2$:$N_2$ (8:92) | 0.5 mol% | 66 |
| 30 bar $O_2$:$N_2$ (8:92) | 0.1 mol% | 67 |
| 60 bar $O_2$:$N_2$ (8:92) | 0.1 mol% | 84 |
| 30 bar $O_2$:$CO_2$ (8:92) | 0.5 mol% | 45 |

**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), 0.5 mol% $H_3PMo_{12}O_{40}$ (7.8 x$10^{-3}$ mmol, 0.014g) or 0.1 mol% $H_3PMo_{12}O_{40}$ (1.56 x$10^{-3}$ mmol, 0.003g), 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) in 1 mL EtOAc under gas mixture at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard.

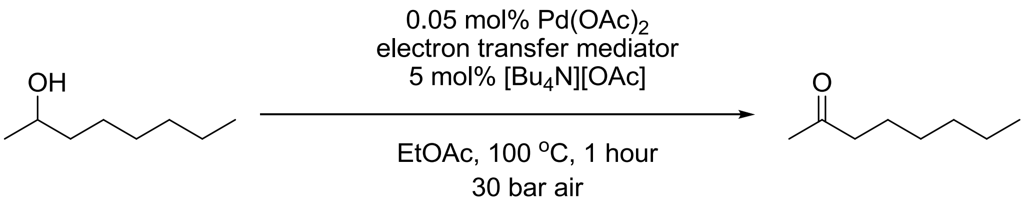
### 2.7 Optimisation of $H_3PMo_{12}O_{40}$ loading



| $H_3PMo_{12}O_{40}$ loading | % yield |
|---|---|
| 0.05 mol%* | 84 |
| 0.1 mol% | 90 |
| 0.5 mol% | 73 |
| 1 mol% | 63 |
| 2 mol% | 38 |

**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ (7.8 x$10^{-4}$ mmol, 1.75 x$10^{-4}$ g), $H_3PMo_{12}O_{40}$ as described, 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) in 1 mL ethyl acetate under 30 bar pressurized air at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard. * For loading of 0.05 mol% $H_3PMo_{12}O_{40}$ the reaction was scaled up by a factor of 5 to facilitate weighing of small amounts of polyoxometalate. We also confirmed at this scale that 0.1 mol% $H_3PMo_{12}O_{40}$ gave the same result as obtained on the smaller scale.

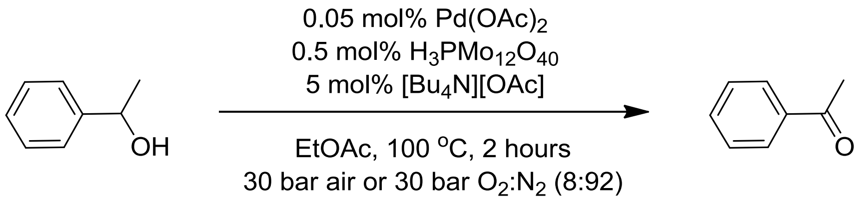
### 2.8 Comparison of electron transfer mediators

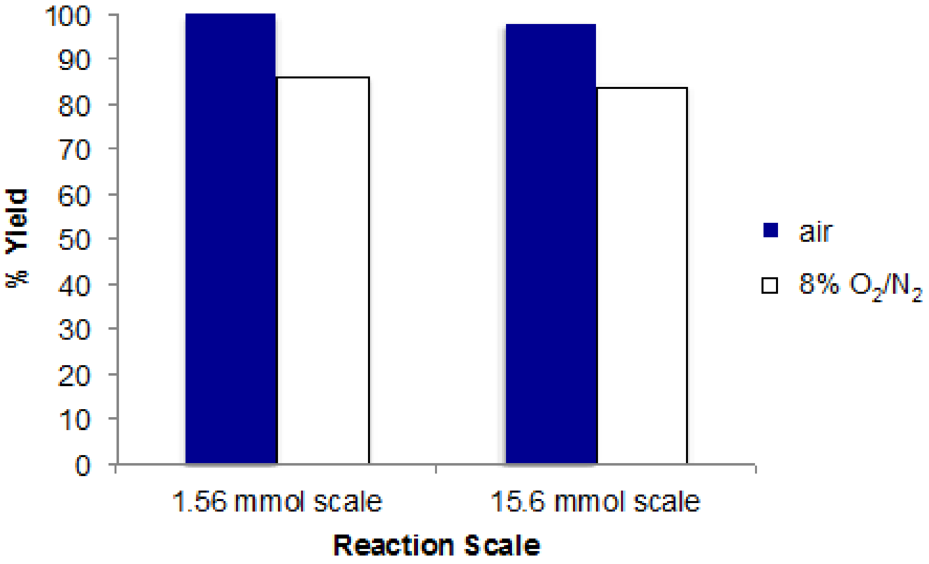


| Electron Transfer Mediator | % yield |
|---|---|
| none | 24 |
| 0.5 mol% $H_3PMo_{12}O_{40}$ | 73 |
| 0.1 mol% $H_3PMo_{12}O_{40}$ | 90 |
| 0.1 mol% $H_3PW_{12}O_{40}$ | 46 |
| 0.1 mol% $H_5PV_2Mo_{10}O_{40}$ | 67 |
| 1.2 mol% $MoO_3$ | 70 |
| 1.2 mol% $MoO_3$ + 0.1 mol% $H_3PO_4$ | 82 |
| 1.2 mol% $Cu(OAc)_2$ | 9 |
| 1.2 mol% $CuCl_2$ | 9 |
| 50 mol% $Cu(OAc)_2$ | 3 |
| 1.2 mol% benzoquinone | 1 |
| 50 mol% benzoquinone | 0 |

**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% Pd(OAc)$_2$ (7.8 x10$^{-4}$ mmol, 1.75 x10$^{-4}$ g), electron transfer mediator as described, 5 mol% [Bu$_4$N][OAc] (0.078 mmol, 0.024g) in 1 mL EtOAc under 30 bar of air at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard.

### 2.9 Larger scale reactions

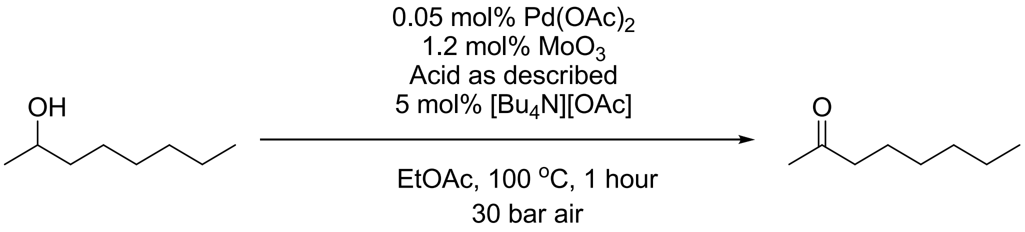


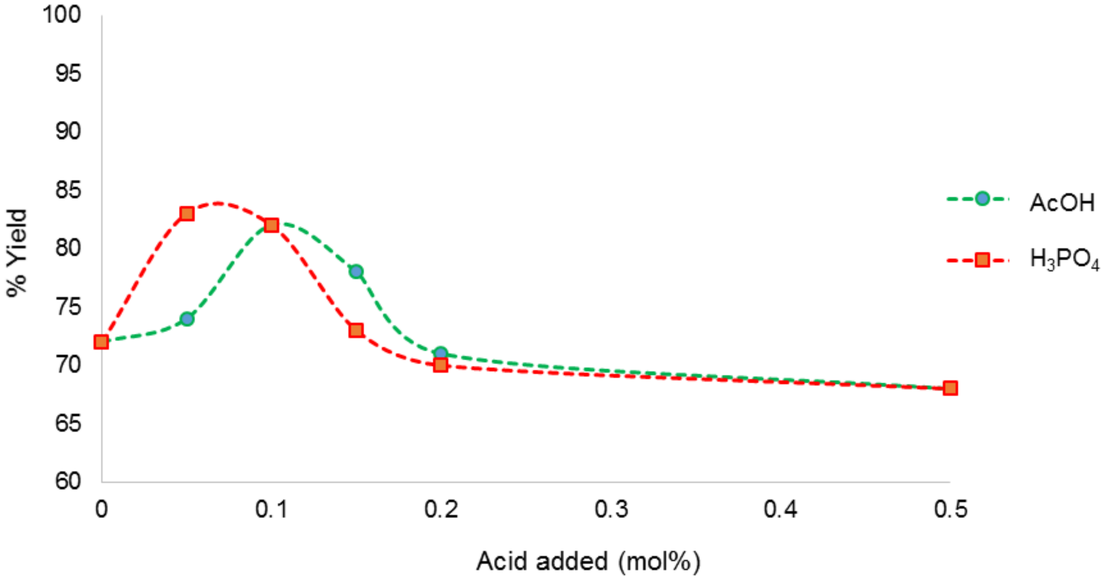


**Conditions:** 1-phenylethanol under both $O_2$:$N_2$ (8:92) and air. The reactions were carried out with 0.05 mol% $Pd(OAc)_2$, 0.5 mol% $H_3PMo_{12}O_{40}$ and 5 mol% $[Bu_4N][OAc]$ under 30 bar of the gas mixture. The 1.56 mmol reactions were carried out in 1 mL of ethyl acetate and the 15.6 mmol reactions were carried out in 30 mL solvent.

## 2.10 Effect of Acid on Pd/$MoO_3$ catalysed aerobic alcohol oxidation

It has been previously suggested that $H_3PMo_{12}O_{40}$, in dilute solution, can undergo decomposition to $H_3PO_4$ and Mo salts. Reaction of $Pd(OAc)_2$ with $MoO_3$ (1.2 mol%, moles of Mo equivalent to 0.1 mol% $H_3PMo_{12}O_{40}$) results in 70% yield of 2-octanone product. We then examined the effect of adding acid to these $MoO_3$ reactions, examining varying concentrations of phosphoric acid and acetic acid. These are both shown to aid the reaction when present in small quantities.





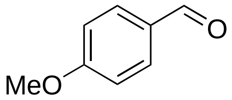
**Conditions**: 1.56 mmol 2-octanol substrate, 0.05 mol% $Pd(OAc)_2$ ($7.8 \times 10^{-4}$ mmol, $1.75 \times 10^{-4}$ g), 1.2 mol% $MoO_3$ ($1.87 \times 10^{-2}$ mmol, 0.0027g), 5 mol% $[Bu_4N][OAc]$ (0.078 mmol, 0.024g), acid loading as described in 1 mL EtOAc under gas mixture at 100 °C for 1 hour. Yield is GC yield in reference to biphenyl internal standard.

## 3 Experimental

### 3.1 Typical procedure for substrate scope (0.05 mol% Pd loading)

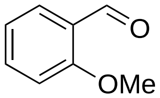
A stock solution of $Pd(OAc)_2$ (0.011g, 0.049 mmol) in 25 mL ethyl acetate was prepared and the solution was placed in a sonicator until the solution was completely homogenous. To a glass lined 16 mL reactor body was added $H_3PMo_{12}O_{40}$ (1.56 x$10^{-3}$ mmol, 0.003 g) and [$Bu_4N$][OAc] (0.078 mmol, 0.024g) and $Pd(OAc)_2$ stock solution (0.4 mL, 7.8 x$10^{-4}$ mmol) and an additional 0.6 mL ethyl acetate. A known amount of biphenyl internal standard was then added (~0.05g) followed by 1.56 mmol of the desired substrate. The reactor vessel was sealed, charged with 30 bar air and stirred at 100 °C on a temperature-controlled hotplate at a rate of 500 RPM for the time stated. After reaction, the reactor was cooled in an ice bath before being slowly depressurized. For GC yields a sample of the reaction mixture was filtered through a silica plug before being analysed by gas chromatography. For isolated yields, the reaction mixture was extracted several times with diethyl ether and brine. The organic layers were combined, dried with $MgSO_4$ and concentrated on a rotary evaporator. The crude product was purified using flash column chromatography (petroleum ether: ethyl acetate).

### 4-methoxybenzaldehyde (2c)



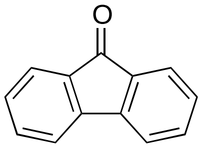
Flash column chromatography (4:1 petroluem ether: ethyl acetate, $R_f$ product = 0.38) yielded **2c** as a colourless oil. Yield = 0.1954g, 92%) $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 9.87 (s, 1H), 7.83 (d, 2H), 7.01 (d, 2H), 3.86 (s, 3H). The spectral properties were in accordance with the literature.[1]

### 2-methoxybenzaldehyde (2d)



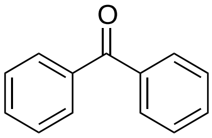
Flash column chromatography (3:1 petroleum ether:ethyl acetate, $R_f$ product = 0.61) yielded **2d** as a colourless oil. Yield = 0.2019g, 95%) $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 10.46 (s, 1H), 7.82 (dd, 1H), 7.63-7,50 (m, 1H), 7.10-6.96 (m, 2H), 3.92 (s, 3H). The spectral properties were in accordance with the literature.[2]

### 9-fluorenone (2q)



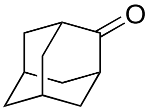
Flash column chromatography (4:1 petroleum ether: ethyl acetate, $R_f$ product = 0.48) yielded **2q** as a yellow crystalline solid. Yield = 0.2612g, 93%) $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 7.67 (dt, 2H), 7.57-7.44 (m, 4H), 7.30 (td, 2H). The spectral properties were in accordance with the literature.[1]

### Benzophenone (2r)



Flash column chromatrography (5:1 petroleum ether: ethyl acetate, $R_f$ product = 0.37) yielded **2r** as a white crystalline solid. Yield = 0.2671g, 94%) $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 7.81 (d, 4H), 7.64-7.54 (m, 2H), 7.49 (t, 4H). The spectral properties were in accordance with the literature.[3]

### 2-adamantanone (2s)



Flash column chromatrography (5:1 petroluem ether: ethyl acetate, $R_f$ product = 0.72) yielded **2s** as a white crystalline solid. Yield = 0.2246g, 96%) $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 2.54 (s, 2H), 2.14-1.91 (m, 12H). The spectral properties were in accordance with the literature.[4]

### 3.2 Typical procedure for substrate scope (0.01 mol% Pd loading)

A stock solution of $Pd(OAc)_2$ (0.011g, 0.049 mmol) in 25 mL ethyl acetate was prepared and the solution was placed in a sonicator until the solution was completely homogenous. To a glass lined 16 mL reactor body was added $H_3PMo_{12}O_{40}$ (1.56 x$10^{-3}$ mmol, 0.003 g) and $[Bu_4N][OAc]$ (0.078 mmol, 0.024g) and $Pd(OAc)_2$ stock solution (0.08 mL, 1.56 x$10^{-4}$ mmol) and an additional 0.92 mL ethyl acetate. A known amount of biphenyl internal standard was then added (~0.05g) followed by 1.56 mmol of the desired substrate. The reactor vessel was sealed, charged with 30 bar air and stirred at 100 °C on a temperature-controlled hotplate at a rate of 500 RPM for the time stated. After reaction, the reactor was cooled in an ice bath before being slowly depressurized. A sample of the reaction mixture was filtered through a silica plug before being analysed by gas chromatography.

### 3.3 Typical procedure for larger scale reactions

A stock solution of $Pd(OAc)_2$ (0.011g, 0.0490 mmol) in 25 mL ethyl acetate was prepared and the solution was placed in a sonicator until the solution was completely homogenous. To a Hasstelloy C276 100 mL Parr pressurised reactor body was added $H_3PMo_{12}O_{40}$ (7.8 x$10^{-2}$ mmol, 0.142g) and $[Bu_4N][OAc]$ (0.78 mmol, 0.235g) in 26 mL ethyl acetate. 15.60 mmol substrate was added and the reactor vessel was heated and stirred (2400 RPM) under ~5 bar air or $O_2$:$N_2$ (8:92) until the temperature stabilized at 100 °C. $Pd(OAc)_2$ in ethyl acetate stock solution (4 mL, 7.8 x$10^{-3}$ mmol) was then added *via* an injector port and flushed through with pressurized air or $O_2$:$N_2$ (8:92) The reactor was held at 30 bar pressure and stirred for the appropriate length of time before being cooled in ice and slowly depressurized. A sample of the reaction mixture was filtered through a silica plug before being analysed by gas chromatography.

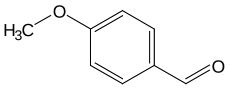
### 3.4 Typical procedure for glassware method

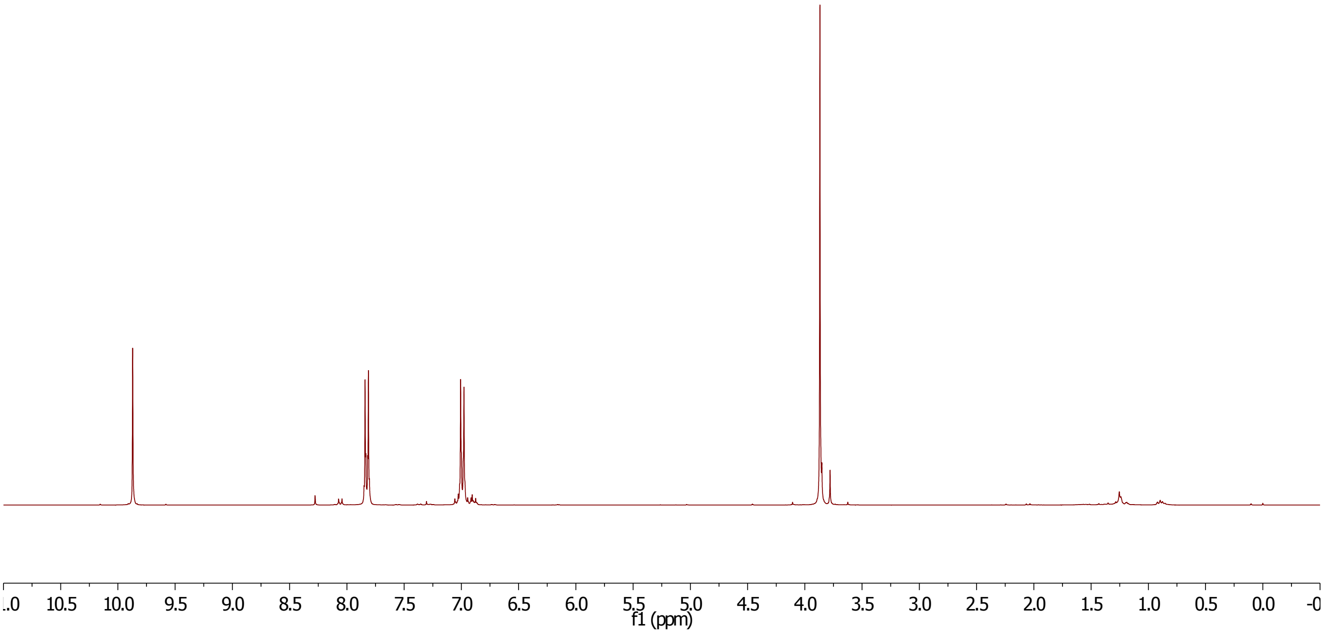
A stock solution of $Pd(OAc)_2$ (0.011g, 0.049 mmol) in 25 mL toluene was prepared and the solution was placed in a sonicator until the solution was completely homogenous. To a 100 mL 2-necked round bottom flask was added $H_3PMo_{12}O_{40}$ (0.039 mmol, 0.071 g) and $[Bu_4N][OAc]$ (0.39 mmol, 0.118g) and $Pd(OAc)_2$ stock solution (4 mL, 7.8 x$10^{-3}$ mmol) and an additional 1mL toluene. A known amount of biphenyl internal standard was then added (~0.1g) followed by 7.8 mmol of the desired substrate. The flask was bubbled with $O_2$ before being heated to 100 °C under reflux with an $O_2$ balloon attached and stirred at 500 RPM for the time stated. After reaction, the flask was cooled in an ice bath. For GC yields a sample of the reaction mixture was filtered through a silica plug before being analysed by gas chromatography. For the isolated yield of camphor, the reaction mixture was poured into a separating funnel and extracted several times with brine and diethyl ether. The organic layers were combined, dried with $MgSO_4$ and concentrated on a rotary evaporator. The crude product was purified through flash column chromatography (10% ethyl acetate in hexanes, product $R_f = 0.72$). The product was isolated as a white crystalline solid. Yield = 1.13g, 96%) $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 2.36 (dt, 1H), 2.09 (t,1H), 2.01-1.89 (m, 1H), 1.85 (d, 1H), 1.75-1.61 (m, 1H), 1.46-1.29 (m, 2H), 0.96 (s, 3H), 0.91 (s, 3H), 0.84 (s, 3H). The spectral properties were in accordance with literature.[5]

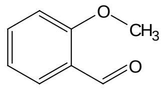
### 3.5 Synthesis of $H_5PV_2Mo_{10}O_{40}$

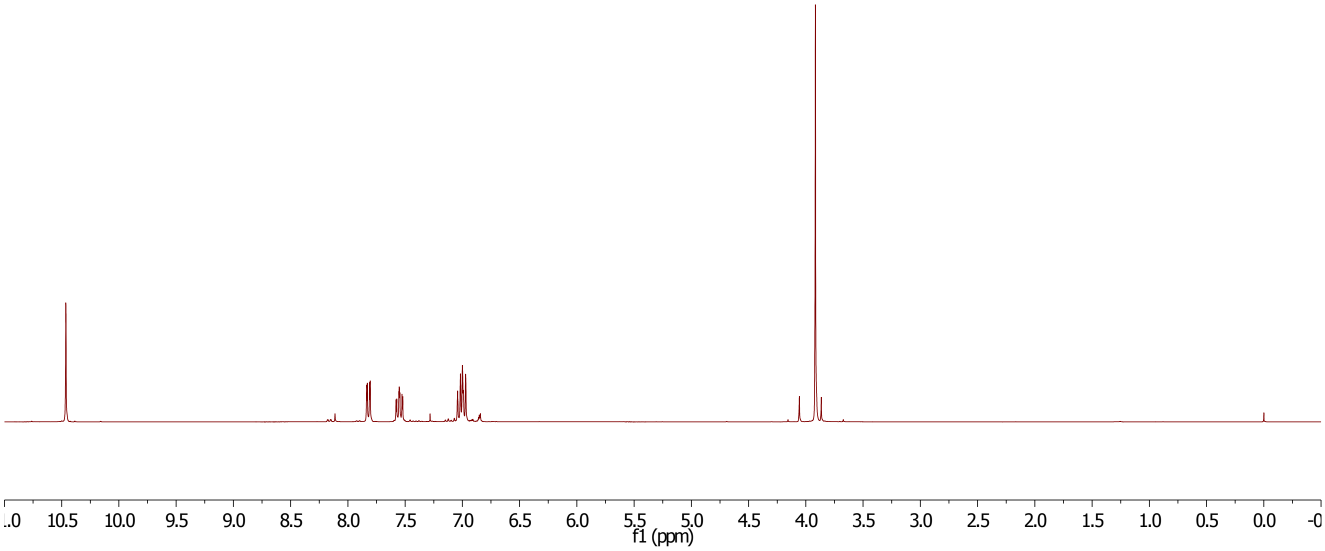
The HPA was prepared according to a literature procedure:[6] To a 500 ml round bottomed flask equipped with a stirrer bar was added 50 ml of distilled water. The water was heated to boiling and sodium metavanadate (12.2 g, 100 mmol) was added. Sodium phosphate dibasic (3.55 g, 25 mmol) in 50 ml distilled water was added and the mixture was allowed to cool to room temperature. Concentrated sulphuric acid (5 ml, 85 mmol) was added dropwise and the green solution turned dark red. The flask was cooled in an ice bath to counteract the heat evolved from the addition of acid. Sodium molybdate (60.5 g, 250 mmol) in 100 ml water was added to the flask under vigorous stirring. The reaction mixture was allowed to stir at room temperature for several minutes before concentrated sulphuric acid (42 ml, 714 mmol) was added dropwise over a period of one hour. The reaction mixture was poured into a separating funnel and extracted several times with 500 ml diethyl ether. A dark red oily lower layer was isolated and air was bubbled through this to remove ether. The product was recrystallised from water, filtered under vacuum and the large red crystals were washed with ice cold water and air dried. 12.58 g of crystals were obtained (26% yield based on P).Thermogravimetric analysis indicated 11 water molecules per polyoxometalate. $^{31}$P NMR ($CD_3COCD_3$, 85% $H_3PO_4$ external standard) -2.23, -1.76, -1.42, -1.05, -0.83. IR 1052, 947, 864 and 739 cm$^{-1}$. Metals analysis: found (calculated) % V 5.00 (5.30), Mo 48.70 (49.60).

## 4 $^1$H NMR spectra of isolated products






O
CH3
O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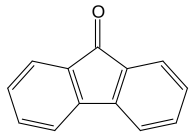
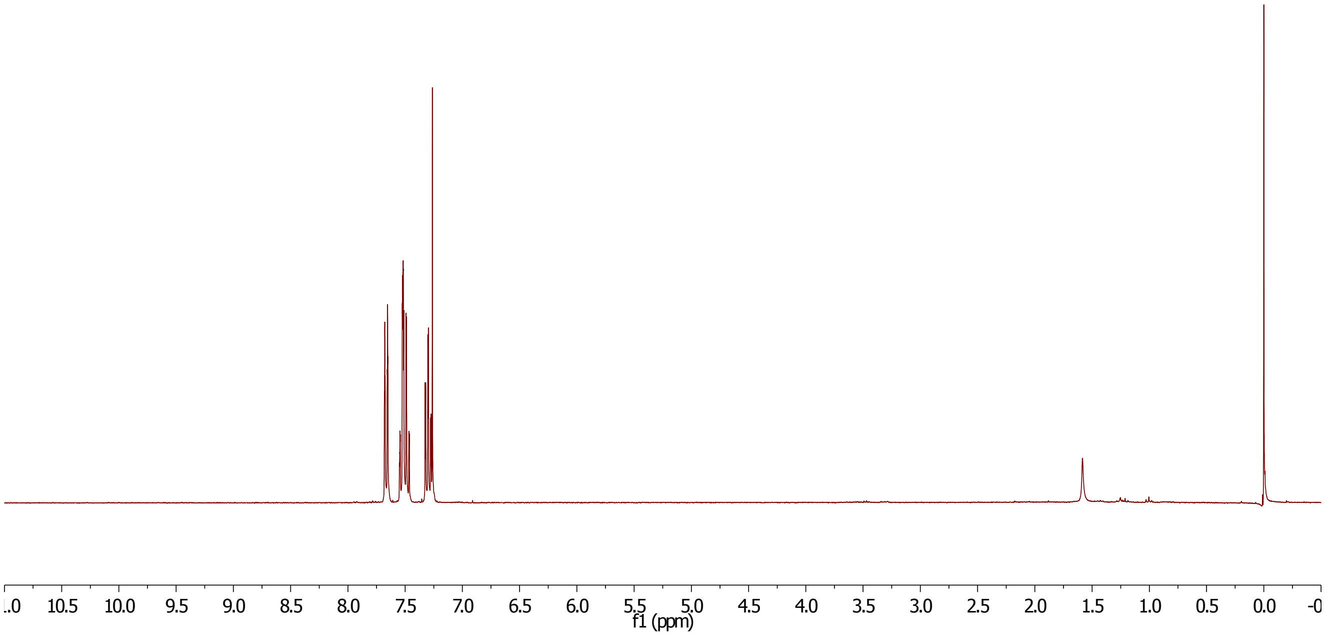
-0
f1 (ppm)


O


.0
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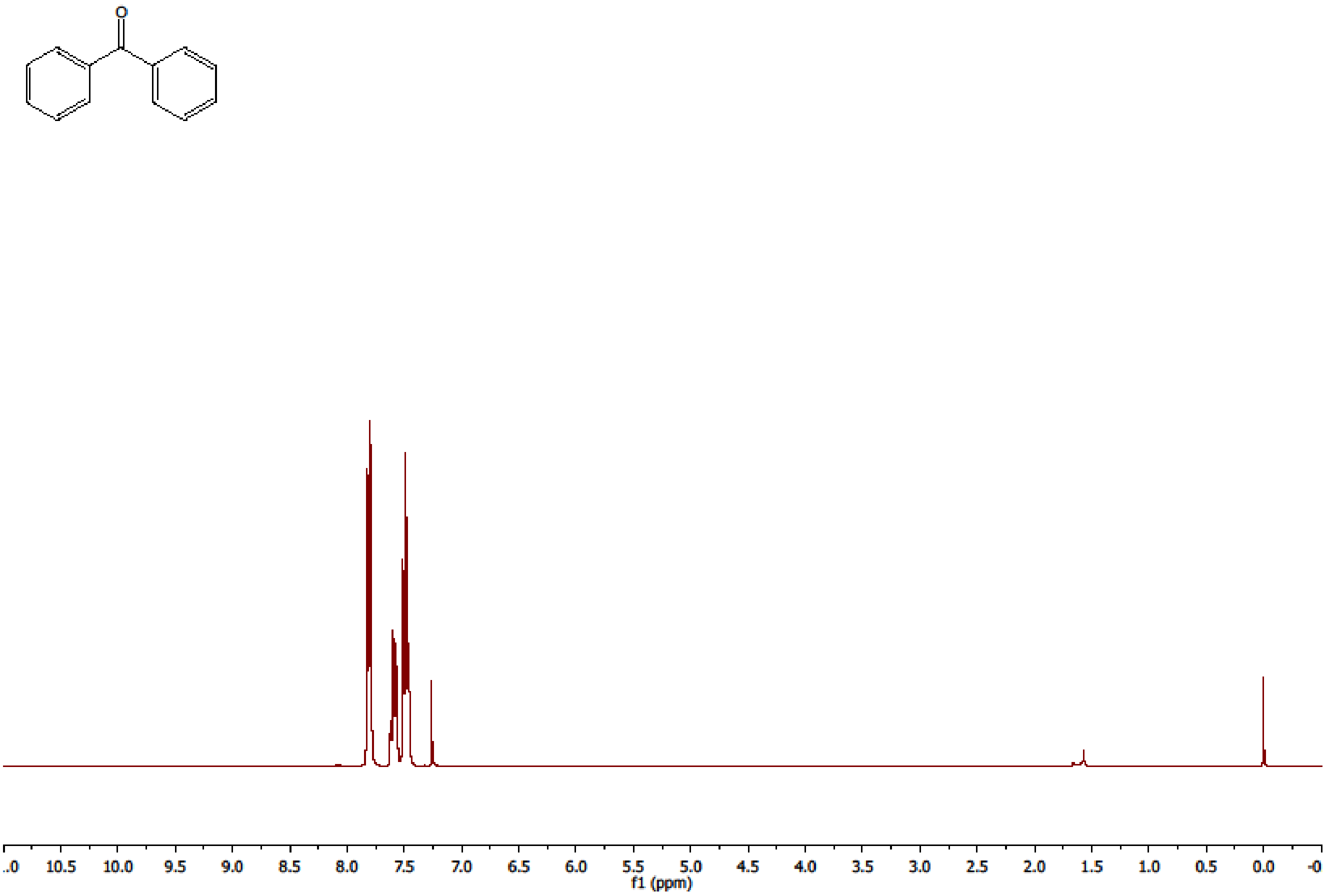
f1 (ppm)


O
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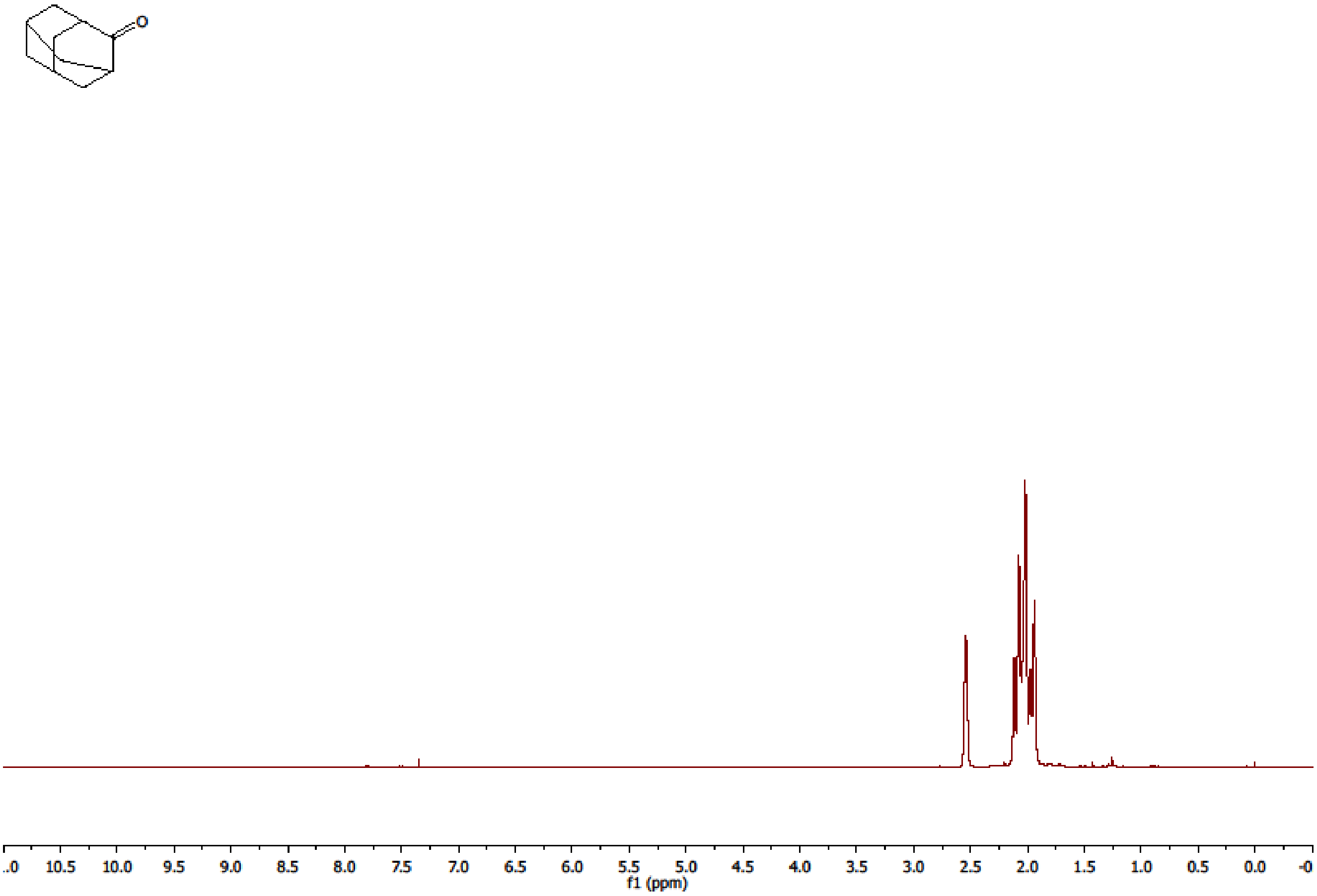
f1 (ppm)


O
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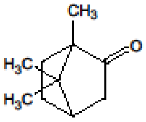
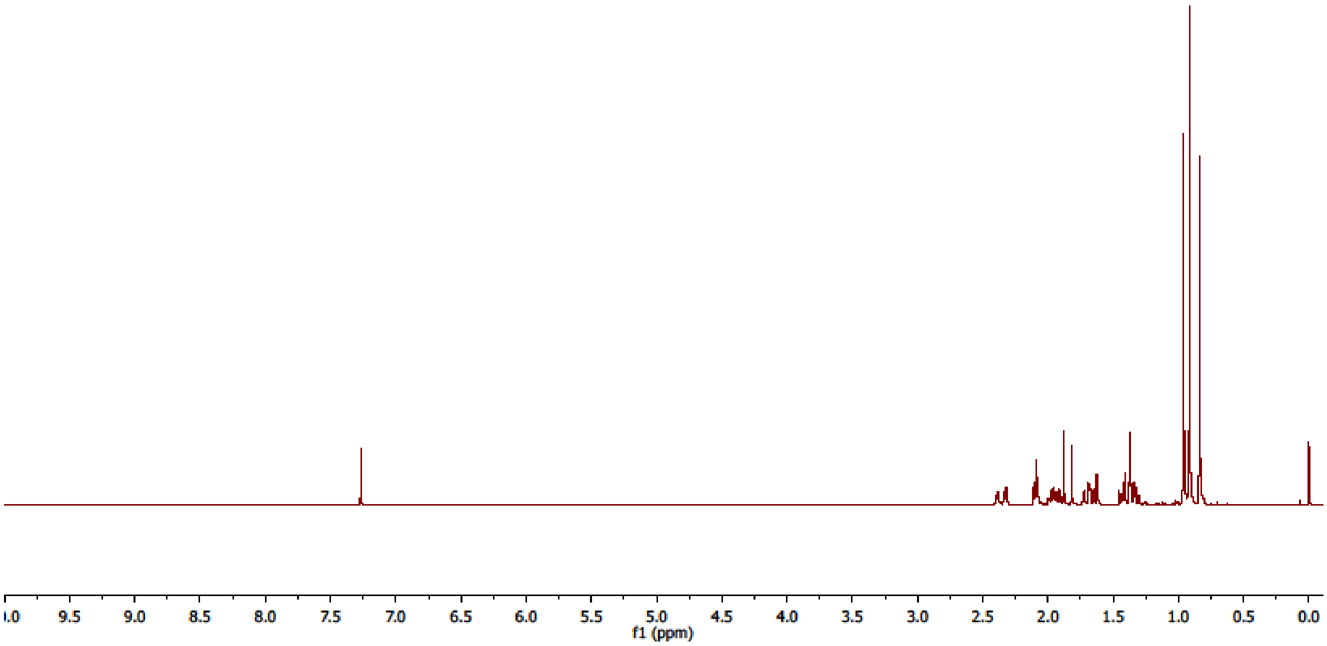
f1 (ppm)





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[1] R. Prebil, G. Stavber and S. Stavber, *Eur. J. Org. Chem.,* 2014, 395.

[2] L. Han, P. Xing and B. Jiang, *Org. Lett.,* 2014, **16**, 3428.

[3] X. Ma, Z. Li, F. Liu, S. Cao and H. Rao, *Adv. Synth. Catal.,* 2014, **356**, 1741.

[4] Y. Sasano, K. Murakami, T. Nishiyama, E. Kwon and Y. Iwabuchi, *Angew. Chem. Int. Ed.,* 2013, **52**, 12624.

[5] M. Iinuma, K. Moriyama and H. Togo, *Eur. J. Org. Chem.,* 2014, 772.

[6] G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem*., 1968, **7**, 437.