# Efficient and selective oxidation of benzylic alcohols to carbonyl compounds using $O_2$ catalysed by $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ under photoirradiation

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Oxidation of a series of various primary and secondary benzylic alcohols with $O_2$ over $[\mathrm{nBu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ as a recyclable and green photocatalyst in $CH_3CN$ resulted in the corresponding aldehydes and ketones selectively in high yields.

**Keywords:** benzylic alcohols, photocatalyst, oxidation, sol–gel technique, silica-supported decatungstate

Photochemical and photoredox properties of isopoly- and heteropolyoxotungstates (POTs) have been extensively investigated.[1] It is well-known that the photocatalytic efficiency of POTs such as $W_7O_{24}^{6-}$, $W_{10}O_{32}^{4-}$, $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$ is comparable to that of the semicoductor $TiO_2$.[2,3] The outstanding photocatalytic ability of these non-toxic and green compounds attributed to the existence of the O→W CT band in their UV–Vis absorption spectra. Hence, illumination of POTs at this band generates a strongly oxidising excited state which can accept a certain number of electrons. Their ability to undergo photo-induced multielectron transfer without decomposition is attractive for their use as effective photocatalysts in the oxidation of organic substrates. After oxidising an organic substrate, the photoreduced form of POT is usually reoxidised to its original oxidation state by an electron acceptor such as dioxygen. This reaction is the basis for the photocatalytic action of POTs.[1]

Among the various POTs, decatungstate ($W_{10}O_{32}^{4-}$) presents an interesting case in that its O→W CT absorption band at the W–O–W bond is at a higher wavelength (324 nm) than at least the 12-tungstates (*ca* 265 nm).[1,4] Thus, transition from the ground state to the excited state is easier for $W_{10}O_{32}^{4-}$ than for the 12-tungstates. Otherwise, photoreducton of $W_{10}O_{32}^{4-}$ in the presence of organic compounds produces a directly reduced blue species ($W_{10}O_{32}^{5-}$) which is reoxidised more rapidly by $O_2$. For these reasons, photoexcited decatungstates such as $Na_4W_{10}O_{32}$ and $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$ in the presence of $O_2$ as a reoxidising reagent have been extensively used for oxidation of a variety of organic compounds *e.g.* hydrocarbons, aliphatic alcohols, alkyl benzenes, amides, amines, aliphatic carboxylic acids and thioethers in homogeneous systems.[5-17] However, it is still difficult to separate these POTs from reaction mixtures because of their high solubility in polar media such as $H_2O$ and $CH_3CN$, which impedes ready recovery and reuse of them. Therefore, considerable attention has been focused recently on heterogenisation of POTs into inorganic solid networks such as silica and zeolites for synthetic purposes in organic chemistry.[18-20] These systems make POTs easily handled and recycled.

In view of the interest in the heterogenisation of POTs, we now report on the use of silica-supported decatungstate, $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$, as a heterogeneous photocatalyst for oxidation of a variety of benzylic alcohols under $O_2$. As far as we know, there is no report regarding the photocatalytic application of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$, especially under heterogeneous conditions for the oxidation of these substrates by $O_2$.

At first, the $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ composite was prepared by entrapment of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$ into a silica matrix via a sol–gel technique involving the hydrolysis of tetraethylorthosilicate ($Si(OEt)_4$, TEOS) as the $SiO_2$ source according to the reported procedure.[21,22] During the hydrolysis of TEOS in the presence of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$, the $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$ molecules are entrapped in silica matrix.

The photocatalytic activity of the $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ was first tested by the oxidation of benzhydrol. We observed that when a heterogeneous mixture of this alcohol and a catalytic amount of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ in acetonitrile was irradiated under an $O_2$ atmosphere, the benzophenone formed as the only photoproduct in 82 % yield within 1.25 h. Using pure $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$, not encapsulated in the silica, we found that 80 % of the benzhydrol was oxidised to benzophenone within 2.25 h under same conditions. Also, when the pure $SiO_2$ support was used as a catalyst for aerobic oxidation of benzhydrol, no oxidation product was detected from GC analysis after 4 h irradiation, suggesting that the photocatalytic activity of the $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ system is only due to that $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$.

Control reactions in the absence of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ and light did not result in any product. On the other hand, when a suspension of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ in acetonitrile in the presence of bezhydrol was irradiated under $N_2$, it rapidly became blue, indicating the formation of reduced decatungstate.[6,8] Under these conditions, GC analysis indicated that a trace amount of benzophenone (< 5%) was obtained and about 95% of the starting benzhydrol was recovered even after a longer irradiation time (6 h). This observation confirmed that $O_2$ plays an important role in the reoxidation of the reduced form of decatungstate and therefore, in completion of photocatalytic cycle.

Separation and recovery of the $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ is easy; the photocatalyst is separated by simple filtration after the reaction. At the same time, the concentration of W in the filtrate was determined as less than 1 % by ICP–AES. Indeed, the recovered photocatalyst was recycled and deactivation of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ was hardly observed in oxidation of benzhydrol even after eight catalytic cycles. On the other hand, in an experiment when the catalyst separated from the reaction mixture shortly (30 min) after beginning the irradiation and the reaction filtrate was further irradiated under $O_2$, no extra formation of benzophenone was observed by GC and TLC even after 4 h. All these findings confirmed that the present photoreaction catalysed by $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ is heterogeneous in nature. Therefore, although during this study we found that the pure $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$ in a homogeneous system also catalyses the oxidation of benzylic aclcohols such as benzhydrol to benzophenone in a efficient way under $O_2$ (see above), our results have focused on oxidation of these substrates in the presence of the $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ system which permits recycling and reuse of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}$.

Under similar conditions as for benzhydrol, the photolysis of a series of primary and secondary benzylic alcohols (**1**) in the presence of $[n\mathrm{Bu}_4\mathrm{N}]_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ was studied. We found that these substrates are efficiently oxidised to the corresponding carbonyl compounds (**2**) in high yield without overoxidation of the benzaldehydes to the carboxylic acids. The results

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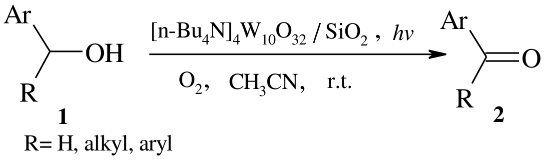

R= H, alkyl, aryl

**Scheme 1**

are summarised in the Table. These results can be explained on the basis of the reaction in Scheme 1.

As seen in Table 1, to evaluate the scope and limitations of this method, the oxidation of a variety of ring-substituted primary and secondary benzylic alcohols having various electron-donating and –withdrawing groups e.g. Me-, *i*-Pr, *t*-Bu-, –OMe, halogen, $–NO_2$ and $-CF_3$ was investgated with $O_2$ over $[n Bu_4N]_4W_{10}O_{32}/SiO_2$. All of these alcohols were selectively converted into their corresponding aldehydes and ketones in moderate to high yields (entries 1–19). Other arylcarbinols gave the corresponding aldehydes in good yields (entries 20–22). Furthermore, heterocyclic alcohols are also selectively oxidised to the corresponding aldehydes without oxidation of heteroatoms like N, S (entries 23–25). With cinnamyl alcohol, an allylic alcohol, a similar result was obtained and its photolysis in the presence of $[n Bu_4N]_4W_{10}O_{32}/SiO_2$ led to oxidation only of the alcoholic moiety whereas the double carbon–carbon bond remained intact (entry 26).

To study the chemoselectivity, a mixture of 1-phenylethanol and 2-phenylethanol was next subjected to photoirradiation in the presence of $[n Bu_4N]_4W_{10}O_{32}/SiO_2$ under $O_2$ within 1 h, GC confirmed that the former oxidised to acetone in *ca* 84 % yield and the latter gave 2-phenylacetaldehyde in < 5 % yield. These studies clearly reveal that the present method can be applied for the chemoselective oxidise benzylic alcohols in the presence of non-benzylic alcohols. This test prompted us to oxidation of some of *vic*-diols containing benzylic and non-benzylic OH groups under the present catalytic oxidation system. It was observed that in these alcohols only the benzylic hydroxy group is efficiently converted into the carbonyl group under appropriate irradiation time (entries 27–30). Therefore, this method is selective for the oxidation of benzylic OH in the presence of non-benzylic OH.

It is noteworthy for comparison that several groups have studied the aerobic photocatalytic oxidation of unactivated aliphatic alcohols *e.g.* ethanol and 2-propanol by $[nBu_4N]_4W_{10}O_{32}$ but most of their work focused on the mechanistic aspects of photocatalysis by this POT.[1,4,8,10] However, their reported results indicate that these alcohols are much less reactive to oxidation. For example, 2-propanol was converted into acetone with 22 % yield after 30 h irradiation in acetonitrile under $O_2$ and in the presence of $[n Bu_4N]_4W_{10}O_{32}$.[8] In contrast to aliphatic alcohols, we have discovered here that various activated (benzylic and allylic) alcohols are more reactive to oxidation by $[n Bu_4N]_4W_{10}O_{32}$ under $O_2$.

By combination of the above facts and the results presented in Table 1, together with literature data,[5-17] the course of events following light absorption by $W_{10}O_{32}^{4-}$ in $[n Bu_4N]_4W_{10}O_{32}/SiO_2$ composite can be explained by the plausible mechanism given below using benzhydrol ($Ph_2CHOH$) as a prototype substrate (Scheme 2).

It seems that the formation of the one-electron reduced of decatungstate, $W_{10}O_{32}^{5-}$, in the presence of an alcoholic substrate involves hydrogen-atom abstraction from the alcohol by photoexcited decatungstate, $W_{10}O_{32}^{4-*}$, followed by rapid electron transfer. On this basis, photooxidation of alcohols is mainly due to hydrogen transfer rather than electron transfer. The following facts confim this mechanism: (a) when the tertiary benzylic alcohols such as triphenylmethanol and

$$2\,W_{10}O_{32}^{4-} \xrightarrow{hv} 2\,W_{10}O_{32}^{4-*}$$

$$Ph_2CHOH + W_{10}O_{32}^{4-*} \longrightarrow \dot{P}h_2C\text{-}OH + (W_{10}O_{32}^{5-} + H^+) \text{ or } HW_{10}O_{32}^{4-}$$

$$Ph_2\dot{C}\text{-}OH + W_{10}O_{32}^{4-*} \longrightarrow Ph_2C{=}O + W_{10}O_{32}^{5-} + H^+$$

$$2W_{10}O_{32}^{5-} + 1/2\,O_2 + 2H^+ \longrightarrow 2\,W_{10}O_{32}^{4-} + H_2O$$

$$\text{net: } Ph_2CHOH + 1/2\,O_2 \xrightarrow[W_{10}O_{32}^{4-}]{hv} Ph_2C{=}O + H_2O$$

**Scheme 2** The plausible mechanism for photocatalytic oxidation of benzylic alcohols by $W_{10}O_{32}^{4-} \equiv [n Bu_4N]_4W_{10}O_{32}/SiO_2$.

**Table 1** Oxidation of various benzylic alcohols with $O_2$ catalysed by $[n Bu_4N]_4W_{10}O_{32}/SiO_2$ under photoirradiation.

| Entry | Alcohol | Product[a] | Time/ h[b] | Yield/ %[c] |
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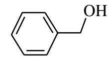
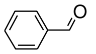
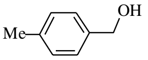
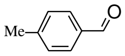
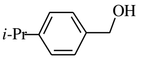
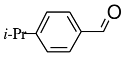
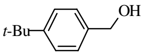
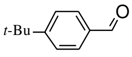
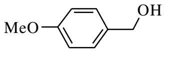
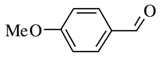
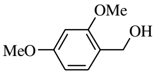
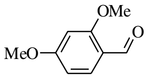
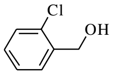
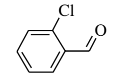
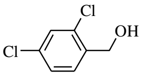
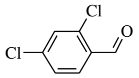
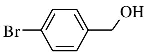
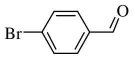
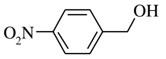
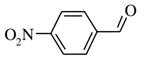
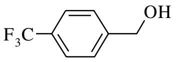
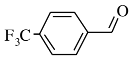
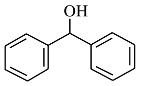
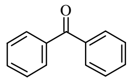
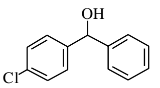
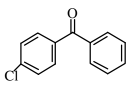
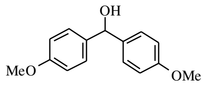
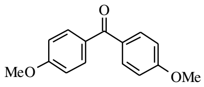
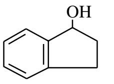
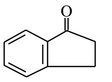
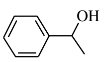
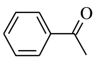
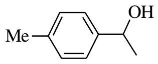
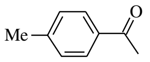
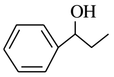
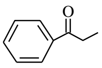
| 1 |  |  | 2 | 80 |
| 2 |  |  | 1.25 | 92 |
| 3 |  |  | 1.25 | 94 |
| 4 |  |  | 1.5 | 80 |
| 5 |  |  | 1 | 80 |
| 6 |  |  | 1 | 88 |
| 7 |  |  | 2 | 75 |
| 8 |  |  | 1.25 | 85 |
| 9 |  |  | 1 | 85 |
| 10 |  |  | 3.6 | 55 |
| 11 |  |  | 4 | 60 |
| 12 |  |  | 1.25 | 82 |
| 13 |  |  | 1.25 | 86 |
| 14 |  |  | 1.25 | 90 |
| 15 |  |  | 1 | 86 |
| 16 |  |  | 1 | 85 |
| 17 |  |  | 1 | 95 |
| 18 |  |  | 1 | 84 |

**Table 1** *continued*

| Entry | Alcohol | Product[a] | Time/h[b] | Yield/%[c] |
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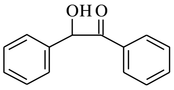
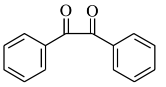
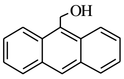
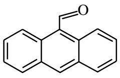
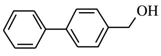
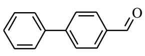
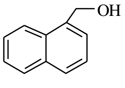
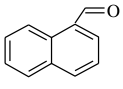
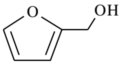
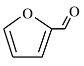
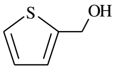
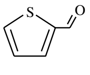
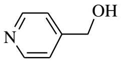
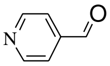
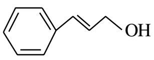
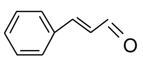
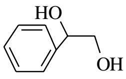
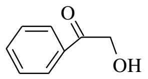
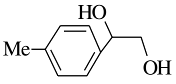
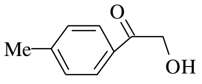
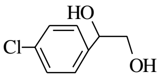
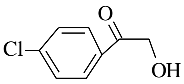
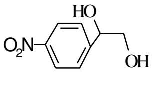
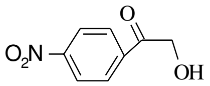
| 19 |  |  | 1.5 | 65 |
| 20 |  |  | 1.5 | 78 |
| 21 |  |  | 3.25 | 66 |
| 22 |  |  | 2 | 76 |
| 23 |  |  | 2.5 | 76 |
| 24 |  |  | 2.5 | 78 |
| 25 |  |  | 2.5 | 75 |
| 26 |  |  | 1.5 | 80 |
| 27 |  |  | 1.25 | 75 |
| 28 |  |  | 1 | 90 |
| 29 |  |  | 1.25 | 82 |
| 30 |  |  | 4 | 62 |

[a]All products were characterised on the basis of mass, IR and $^1$H NMR spectral data and comparison with those of authentic samples or reported data. [b]Irradiation time. [c]Isolated yields

2-phenyl-2-propanol which possess no H-atom at the benzylic position, were examined as substrates under the our reaction conditions, the starting materials were recovered quantitively even after 6 h irradiation. (b) Also, the observation above that 1-phenylethanol reacts very much faster than 2-phenylethanol is also consistent with a hydrogen-atom abstraction mechanism. (c) Indeed, Ward *et al.*'s work[21] supports this mechanism, showing a deuterium isotope effect in acetone production, $k_H/k_D = 3.7$, when deuterated $Me_2CDOH$ is photolysed with $Mo_7O_{24}^{6-}$.

According to this plausible mechanism, species with a high reactivity for oxidation will have easily removable or abstractable H-atoms. Therefore, primary and secondary alcohols with benzylically activated C–H bonds in the present work act as good photoreducing reagents and are oxidised in an efficient way. Also, the observed selectivity for the oxidation of *vic*-diols at the benzylic position can be attributed to the ease of dissociation of the benzylic active C–H bond in comparison with non-benzylic C–H bonds.

In conclusion, a novel, synthetically important, efficient and enviromentally benign photocatalytic method is presented for the oxidation of benzylic alcohols to aldehydes and ketones by $O_2$. No other over-oxidised compounds were detected. Benzylic hydroxy groups can be efficiently converted into carbonyl groups in the presence of non-benzylic hydroxy groups. It is noteworthy that the catalyst can be used for subsequent cycles of oxidation without any release of the polytungstate during the experiments, and without any loss of its photocatalytic activity. It seems most likely that the primary reaction between $W_{10}O_{32}^{4-*}$ and the alcoholic substrates involves hydrogen-atom abstraction prior to electron transfer. Studies on the detailed mechanism and also the photocatalytic applications of $[n\text{Bu}_4\text{N}]_4W_{10}O_{32}/SiO_2$ to the oxidation of other organic substrates are now in progress in our laboratory.

## Experimental

The silica-supported decatungstate, $[n\text{Bu}_4\text{N}]_4W_{10}O_{32}/SiO_2$, containing 20% w/w of $[n\text{Bu}_4\text{N}]_4W_{10}O_{32}$, was synthesised by the sol–gel method reported in the literature.[22,23] Also, $[n\text{Bu}_4\text{N}]_4W_{10}O_{32}$ was prepared according to Klemperer method.[24] Alcohols were either purchased commercially or synthesised as reported in the literature.[25,26] Irradiations were carried out with a high-pressure Hanau 400 W mercury lamp using a cutoff filter ($\lambda \geq 310$ nm).

*General procedure for photocatalytic oxidation of benzylic alcohols by using* $[n\text{Bu}_4\text{N}]_4W_{10}O_{32}/SiO_2$ *under* $O_2$

In a Pyrex flask equipped with a magnet bar, a solution of benzylic alcohol (1 mmol) in acetonitrile (25 ml) was prepared. To this solution was added $[n\text{Bu}_4\text{N}]_4W_{10}O_{32}/SiO_2$ (100 mg). The Pyrex flask containing the solution was purged with $O_2$ and joined through an inlet tube to a balloon filled with $O_2$ before irradiation. The reaction mixture was irradiated while its temperature was maintained at 25±2 °C by circulation of water through an external cooling coil. Oxidation of the alcohol was monitored by TLC and/or GC. After a suitable irradiation time, the irradiation was stopped and the *hetero-geneous* photocatalyst, $[n\text{Bu}_4\text{N}]_4W_{10}O_{32}/SiO_2$, separated *via* filtration. The filtrate was concentrated and chromatographed on a silica-gel plate with $CCl_4$–$Et_2O$ as an eluent to give the carbonyl product. Yields are shown in Table 1. The products of entries 1–26 are commercially available and were identified through comparison of their physical and spectral data (m.p., TLC, IR, $^1$H and/or $^{13}$C NMR and MS) with those of authentic samples. The products of entries 27,[27,28] 28,[27] 29[29] and 30[30] were characterised by comparing their m.p., IR, $^1$H NMR and MS spectra data with literature data.

Selected physical and spectral data for some of products listed in Table 1 are as follows for AA'XX' systems, $J^* = J_{23} + J_{25}$)

*p-Methylbenzaldehyde (entry 2)*: Colourless oil; IR (neat): 1701, 1607, 1386, 1308, 1207, 1169, 847, 808 cm$^{-1}$; $^1$H NMR δ: 2.43 (s, 3H), 7.33 (m, $J^*$ = 7.9 Hz, 2H), 7.78 (m, $J^*$ = 7.9 Hz, 2H), 9.97 (s, 1H); $^{13}$C NMR δ: 21.86, 129.73, 129.84, 134.22, 145.55, 191.97; MS *m/z* (rel. int.): 120 (M$^+$, 34), 119 (100), 91 (72), 65 (28).

*p-Nitrobenzaldehyde (entry 10)*: M.p. 105–106 °C (lit: 104–105)[31]; IR (KBr): 1712, 1607, 1538, 1344, 1293, 1196, 854, 819, 738 cm$^{-1}$; $^1$H NMR δ: 8.08 (m, $J^*$ = 8.5 Hz, 2H), 8.41 (m, $J^*$ = 8.5 Hz, 2H), 10.17 (s, 1H); $^{13}$C NMR δ: 124.30, 130.40, 142.20, 151.20, 190.30; MS *m/z* (rel. int.): 151 (M$^+$, 44), 150 (100), 77 (13), 51 (16).

*4-Methylacetophenone (entry 17)*: Colourless oil; IR (neat): 1680, 1405, 1355, 1265, 1180, 1010, 950, 810 cm$^{-1}$; $^1$H NMR δ: 2.41 (s, 3H), 2.58 (s, 3H), 7.26 (m, $J^*$ = 8.2 Hz, 2H), 7.86 (m, $J^*$ = 8.2, 2H); $^{13}$C NMR δ: 21.65, 26.56, 128.47, 129.27, 134.72, 143.91, 198.88; MS *m/z* (rel. int.): 134 (M$^+$, 42), 119 (100), 91 (72), 43 (34).

*Benzil (entry 19)*: M.p. 94–95 °C (lit: 94–95)[31]; IR (KBr): 1727, 1600, 1558, 1344, 1259, 1210, 854, 825 cm$^{-1}$; $^1$H NMR δ: 7.50 (t, *J* = 8.0 Hz, 4H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 4H); $^{13}$C NMR δ: 129.70, 130.50, 133.72, 135.50, 195.32; MS *m/z* (rel. int.): 210 (M$^+$, 30), 105 (100), 77 (64).

*Thiophene-2-carboxaldehyde (entry 24)*: Liquid; IR (neat): 1673, 1300, 1220, 1180, 1010 cm$^{-1}$; $^1$H NMR δ: 7.20 (t, *J* = 3.8 Hz, 1H), 7.70 (m, 2H), 9.90 (s, 1H); $^{13}$C NMR δ: 128.20, 135.00, 136.10, 143.90, 182.80; MS m/z (rel. int.): 112 (M$^+$, 54), 111 (76), 83 (100).

*α-Hydroxyacetophenone (entry 27)*: M.p. 79–80 °C (lit. 80–82 °C)[31]; IR (KBr): 3421, 1689, 1600, 1456, 1409, 1301, 1231, 1106, 970, 761, 683 cm$^{-1}$; $^1$H NMR δ: 3.51 (t, *J* = 4.6 Hz, 1H), 4.89 (d, *J* = 4.6 Hz, 2H), 7.49–7.67(m, 3H), 7.92–7.95 (m, 2H); MS *m/z* (rel. int.): 136 (M$^+$, 15), 105 (77), 77 (100), 59 (17).[27,28]

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## References

1 E. Papaconstantinou, *Chem. Soc. Rev.*, 1989, **18**, 1 and references therein.
2 R.C. Chambers and C.L. Hill, *Inorg. Chem.*, 1991, **30**, 2776.
3 A. Hiskia, A. Mylonas and E. Papaconstantinou *Chem. Soc. Rev.*, 2001, **30**, 62 and references therein.
4 C. Tanielian, *Coord. Chem. Rev.*, 1998, **178–180**, 1165 and references therein.
5 T. Yamase, *Inorg. Chem. Acta*, 1982, **64**, L155.
6 E. Papaconstantinou, *J. Chem. Soc., Chem. Commun.*, 1982, 12.
7 A. Chemseddin, C. Sanchez, J. Livage, J.P. Launay and M. Fournier, *Inorg. Chem.*, 1984, **23**, 2609.
8 K. Momia, Y. Sugie, T. Miyazaki and M. Miwa, *Polyhedron*, 1986, **5**, 1267.
9 T. Yamase and T. Usami, *J. Chem. Soc., Dalton Trans.*, 1988, 183.
10 A. Hiskia and E. Papaconstantinou, *Polyhedron*, 1988, **7**, 477.
11 R.C. Chambers and C.L. Hill, *J. Am. Chem. Soc.*, 1990, **112**, 8427.
12 R.C. Chambers and C.L. Hill, *Inorg. Chem.*, 1991, **30**, 2776.
13 A. Maldotti, R. Amadelli, V. Carassiti and G. Varani, S. Tollari and F. Porta, *Inorg. Chem.,*1994, **33**, 2968.
14 D.C. Duncan, T.L. Netzel and C.L. Hill, *Inorg. Chem.*, 1995, **34**, 4640.
15 A. Mylonas, E. Papaconstantinou and V. Roussis, *Polyhedron*, 1996, **15**, 3211.
16 A. Maldotti, R. Amadelli, V. Carassiti and A. Molinari, *Inorg. Chem. Acta*, 1997, **256**, 309.
17 C.L. Hill and D.A. Bouchard, J. Adelli, A. Sgobino and V. Carassiti, *Inorg. Chem. Acta*, 1998, **272**, 197.
18 A. Molinari, R. Amadelli, L. Andreotti and A. Maldotti, *J. Chem. Soc., Dalton Trans.*, 1999, 1203.
19 R.R. Ozer and J.L. Ferry, *J. Phys. Chem. B*, 2002, **106**, 4336.
20 N. Mizuno and M. Misono, *Cherm. Rev.*, 1998, **98**, 199.
21 M.D. Ward, J.F. Bradjil and R.K. Grasselli, *J. Phys. Chem.*, 1984, **88**, 4210.
22 Y. Izumi, K. Hisano and T. Hida, *Appl. Catal. A: Gen.*, 1998, **181**, 277.
23 Y. Guo, C. Hu, S. Jiang, C. Guo, Y. Yang and E. Wang, *Appl. Catal. B: Environ.*, 2002, **36**, 9.
24 M. Filowitz, R.C.K. Ho, W.G. Klemperer and W. Shun, *Inorg. Chem.*, 1979, **18**, 9310.
25 F. Fringerio, R. Germani, F. Pizzo and G. Sarelli, *Synth. Commun.*, 1989, **19**, 1939.
26 M.A. Reddy, L.R. Reddy, N Bhanumathi and K.R. Rao, *Org. Prep. Proc. Int.*, 2002, **34**, 527.
27 M. Mulbaier and A. Giannis*, Angew. Chem. Int. Ed.*, 2001, **40**, 4393.
28 J.D. Moore and S.N. Finney,*Org. Lett*. 2002*,* **4**, 3001.
29 G. Sorg, A. Mengel, G. Jung and J. Rademann, *Angew. Chem. Int. Ed.*, 2001, **40**, 4395.
30 N.N. Reed, M. Delgado, K. Hereford, B. Clapham and K.D. Janda, *Bioorg. Med. Chem. Lett.* 2002, **12**, 2047.
31 Dictionary of Organic Compounds, 6th ed., Chapman and Hall, London, 1996.