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$Na_4H_3[SiW_9Al_3(H_2O)_3O_{37}]\cdot 12H_2O/H_2O$: a new system for selective oxidation of alcohols with H_2O_2 as oxidant

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Abstract—This work describes a catalytic system consisting of both $Na_4H_3[SiW_9Al_3(H_2O)_3O_{37}]\cdot 12H_2O(SiW_9Al_3)$ and water as solvents (a small quantity of organic solvents were used as co-solvent for a few substrates) that can be good for selective oxidation of alcohols to ketones (aldehydes) using 30% H_2O_2 without any phase-transfer catalyst under mild reaction conditions. The catalyst system allows easy product/catalyst separation. Under the given conditions, the secondary hydroxyl group was highly chemoselectively oxidized to the corresponding ketones in good yields in the presence of primary hydroxyl group within the same molecule, and hydroxides are selectively oxidized even in the presence of alkene. Benzylic alcohols were selectively oxidized to the corresponding benzaldehydes in good yields without over oxidation products in solvent-free conditions. Nitrogen, oxygen, sulfur-based moieties, at least for the cases where these atoms are not susceptible to oxidation, do not interfere with the catalytic alcohol oxidation.

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1. Introduction

The oxidation of alcohols to carbonyl compounds is one of the most frequently used synthetic reactions in organic chemistry and several methods covering a wide variety of reagents have been developed for this important synthetic transformation.[1] In the synthesis of naturally occurring compounds, one usually faces the manipulation of compounds containing several types of functional groups, and it is necessary to selectively oxidize a single group (primary, secondary alcohol or double bond) within the same molecules. Thus, selective transformation of hydroxyl group has been a challenging target for synthetic chemists since it offers an alternative to synthesis via selective protection and deprotection. Many oxidizing reagents are known to promote selective oxidation of secondary alcohols in the presence of primary alcohols,[2,25d] including halogen based oxidants. In these readily available procedures, hydrogen peroxide is an ideal oxidant that has attracted considerable attention in recent years.[1e,2c,3–9] There have been a number of procedures[6–10] for alcohol oxidation using H_2O_2 and in situ generated or preformed metal complexes. However, some of them still need further improvement for their application in the practical organic synthesis. For instance, the systems usually need toxic solvent (affect human health and environment) or phase-transfer catalyst (affect products/catalyst separation).

Over the past decade, polyoxometalates have awoken interest for catalytic oxidations, as they are inherently stable to oxidation. Most notably, Venturello found that $[CH_3(n\text{-}C_8H_{17})_3]_3PO_4[WO(O_2)_2]_4$ displayed a catalytic activity for non-solvent oxidations, although much room was left for improvement. Another especially interesting subclass of polyoxometalates, which are ‘sandwich’ type compounds has shown to be efficient for catalytic oxygen-tranfer reactions,[11–15] e.g. $[Fe(II)_4(PW_9O_{34})_2]^{10-}$ for alkene epoxidation in monophasic systems,[16] $[WZnMn(II)_2(ZnW_9O_{34})_2]^{2-}$ highly active in biphasic alkene epoxidation and alcohol oxidation with H_2O_2.[17,18] Although these polyoxometalate compounds are active in above reaction systems, most of them have disadvantages, for example, need of noxious organic solvents.

In our early work, transition-metal substituent polyoxometalate $Na_6[SiW_{11}ZnH_2O_{40}]\cdot 12H_2O$ was synthesized and used as the catalyst for the oxidation of alcohols.[19] The results suggested that the catalyst $Na_6[SiW_{11}ZnH_2O_{40}]\cdot 12H_2O$ had high catalytic activity. Herein, we report our investigation on the redox activity of non-transition-metal substituent (tri-aluminum) polyoxometalate for oxidation of alcohols; it is very efficient and selective catalyst for oxidation of

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alcohols with H_2O_2. The reaction can be carried out under organic–aqueous biphasic conditions or organic–solvent-free conditions.

2. Results and discussion

2.1. Effect of catalyst on the oxidation of cyclohexanol

Initially, oxidation of cyclohexanol was used as the model reaction to test the activity of various catalysts. The results were shown in Table 1, which were obtained after 7 h of reactions using 2 μmol of the catalysts (SiW_9Al_3, SiW_9Ga_3, SiW_9In_3, and SiW_9Tl_3), 17 mmol of cyclohexanol, and 30 mmol of 30% aqueous H_2O_2. It was observed that SiW_9Al_3 was the best catalyst for the reaction, and cyclohexanol was completely consumed after 7-h reaction with exclusive selectivity to cyclohexanone. Other catalysts were also capable of catalyzing the model reaction, but their efficiencies seemed to be slightly inferior compared with SiW_9Al_3. Compared with other polyoxometalate catalysts,[20] the catalytic system does not need phase-transfer catalyst; this could be due to amphoteric element Al (or Zn) introduced into polyoxometalate that changes distribution of charges in the pattern different to other transition-metal substituent polyoxometalate catalysts, and changes its redox in reaction system. SiW_9Al_3 was, therefore, chosen as a catalyst for further investigation.

2.2. Reaction of different monofunctional alcohols

A series of alcohols was then reacted by using this remarkably simple procedure and the results are presented in Table 2. The secondary alcohols were all oxidized directly to the corresponding ketones using the catalyst in a short time with excellent yield and selectivity under the solvent-free conditions. Actually, we found that there was no need for phase-transfer reagent, as in the solvent-free oxidations previously described.[8,21] Primary alcohols, for short-chain alcohols, were oxidized to the corresponding organic acid without acetonitrile, and for long-chain alcohols, an ounce of acetonitrile was needed. When reactions were carried out without any organic solvent with long-chain alcohols as substrates, longer time was needed to achieve good yields (Table 2). The same investigation was observed in the solvent-free system described by Noyori.[8]

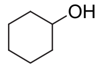
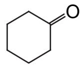
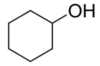
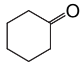
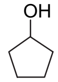
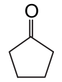
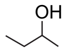
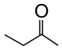
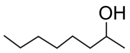
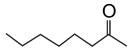
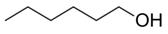
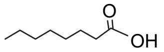
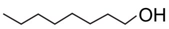
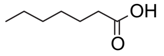
Table 1. Oxidation reaction of cyclohexanol to cyclohexanone with hydrogen peroxide as an oxidant and without solvent[a]

Entry	Catalyst	Product (yield %)
1	SiW_{12}	0
2	SiW_9	0
3	SiW_9Al_3	100
4	SiW_9Al_3[b]	62
5	—	0
6	SiW_9Ga_3	27
7	SiW_9In_3	33
8	SiW_9Tl_3	18
9	$AlCl_3$	0
10	$Al(NO_3)_3$	0

[a] Reactions were carried out with 17 mmol of the alcohol at 90 °C, with 2 μmol of catalysts, and 30 mmol of 30% aqueous H_2O_2 for 7 h.

[b] Catalysts (1 μmol).

Table 2. Oxidation of alcohols with hydrogen peroxide catalyzed by SiW_9Al_3 in acetonitrile or without solvent

Entry	Substrates	Solvent	Time	Products (yield %)
1		—	7	 (99)
2[a]		—	7	 (97)
3		—	8	 (99)
4		—	7	 (99)
5		Acetonitrile	9	 (99)
6		—	10	 (78)
7		Acetonitrile	12	 (61)

Reaction conditions: 17 mmol of substrate, 2 μmol of catalyst, and 50 mmol of H_2O_2 (30%); temperature: 90 °C; time: 7–12 h.

[a] The fifth run.

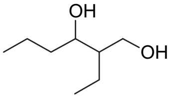
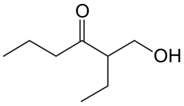
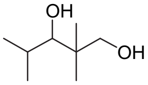
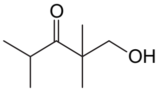
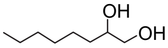
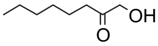
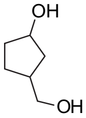
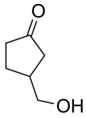
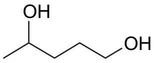
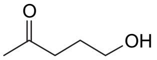
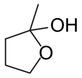
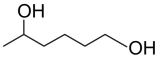
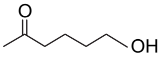
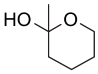
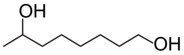
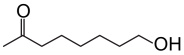
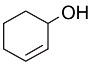
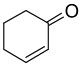
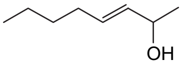
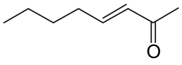
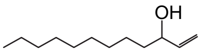
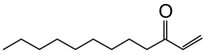
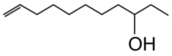
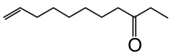
2.3. Selective oxidation of diols and enols

The results of oxidation for a variety of diols and enols using H_2O_2 as oxidant are given in Table 3. The observed transformations were chemoselective when both the primary and secondary hydroxyl groups were present within the same molecules (Table 3). The ketones with the primary alcohol untouched were obtained in good yields. For instance, 2-ethyl-1,3-hexanediol, 2,2,4-trimethyl-1,3-pentanediol, and 1,2-octanediol were all rather effectively oxidized to 1-hydroxy-ketone without the formation of byproducts. In these cases, some lactones (five- or six-membered ring lactone) were also formed as minor products. For instance, 1,4-pentanediol, 1,5-hexanediol, and 1,7-octanediol were oxidized to 1-hydroxy-4-pentanone, 1-hydroxy-5-hexanone, and 1-hydroxy-7-octanone with a little lactones in the obtained products. The result indicated that the catalytic system was highly active in selective oxidation of the compounds with both primary and secondary hydroxyl moieties. Trost and Masuyama[22] found the same selectivity in a molybdenum catalyzed alcohol oxidation by hydrogen peroxide. Alkenols, for instance, 3-octen-2-ol, 1-dodecen-3-ol, and 10-undecen-3-ol were all efficiently oxidized to the corresponding alkenones (alkene aldehyde) in high yields. Allylic alkenols (reactions at low temperature) were more reactive than non-allylic alkenols (reactions at 60 °C). It was worth noting that no epoxide of alkenol was detected in alkenol oxidations. It showed that the catalyst was highly active and selective for oxidation of diols and enols.

2.4. Selective oxidation of benzylic alcohols and heterocyclo compounds

Benzylic alcohols were selectively oxidized to the corresponding benzaldehydes in moderate to good yields without over oxidation under solvent-free conditions. Likewise,

Table 3. The selective oxidation of alcohols with H_2O_2 catalyzed by SiW_9Al_3 in acetonitrile or without solvent

Substrate	H_2O_2 (mmol)	Solvent	Temp (°C)	Time (h)	Conv. (%)	Product (select. %)
	50	—	90	9	100	 (99)
	50	—	90	7	100	 (99)
	50	—	90	9	100	 (99)
	50	—	90	9	100	 (99)
	50	—	90	9	100	 (62)  (37)
	50	—	90	9	100	 (63)  (35)
	50	—	90	9	100	 (99)
	40	—	70	7	100	 (92)
	30	Acetonitrile	60	5	100	 (89)
	30	Acetonitrile	60	7	100	 (76)
	50	Acetonitrile	90	9	100	 (99)

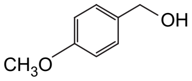
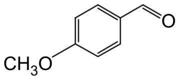
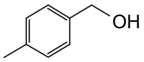
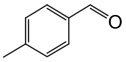
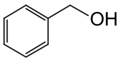
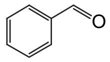
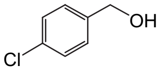
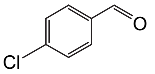
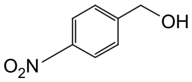
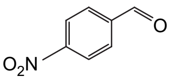
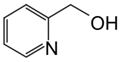
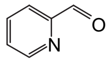
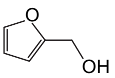
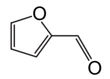
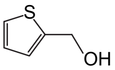
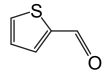
Reaction condition: substrate 20 mmol, catalyst 1.7 μmol, temperature 60–95 °C, and 30–50 mmol of 30% solution of H_2O_2.

furfurol, thiophene-2-methanol, and pyridine-2-methanol were oxidized to furfural, 2-thiophenecarboxaldehyde, and 2-pyridinecarboxaldehyde in high yields, respectively. No oxidation was observed at the N-atom of pyridine-2-methanol and S-atom of thiophene-2-methanol (Table 4).

3. Conclusions

In conclusion, organic-solvent-free oxidations of alcohols using aqueous hydrogen peroxide as an oxidant and SiW_9Al_3 as catalyst provides a general, safe, and simple method for monofunctional alcohols oxidation. Furthermore, secondary alcohols are selectively oxidized even in the presence of primary ones and hydroxides are selectively oxidized even in the presence of alkene. This may be due to amphoteric element Al (or Zn) introduced into polyoxometalate that changes distribution of charges in the pattern different to other transition-metal substituent polyoxometalate compound catalysts. The important advantage of this method, besides the organic-solvent-free conditions for most of substrates, is that it does not require a phase-transfer catalyst. In addition, the catalytic system offers the advantages of simplified workup procedure and recycling.

Table 4. The selective oxidation of alcohols with H_2O_2 catalyzed by SiW_9Al_3 in acetonitrile or without solvent

Substrate	H_2O_2 (mmol)	Solvent	Temp (°C)	Time (h)	Conv. (%)	Product (select. %)
	30	—	90	6	100	 (99)
	30	—	90	7	100	 (99)
	30	—	90	5	100	 (99)
	30	—	90	6	100	 (99)
	30	—	90	12	74	 (99)
	30	—	90	5	100	 (99)
	30	—	90	2	100	 (99)
	30	—	90	4	100	 (99)

Reaction condition: substrate 20 mmol, catalyst 1.7 μmol, temperature 60–95 °C, and 30–50 mmol of 30% solution of H_2O_2.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were measured on a JEOL JNM-A400 NMR spectrometer at 400 and 100 MHz, respectively. The chemical shifts of ^1H NMR spectra are reported in parts per million on δ scale downfield from tetramethysilane used as an internal standard and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. The chemical shifts of ^{13}C NMR spectra are reported in parts per million with chloroform-*d* as an internal standard. Gas chromatographic analyses were carried out using an Agilent6890N/5973N/GC–MS (column: HP-1 100% dimethylpolysiloxane 30 mm×320 mm×0.25 mm) and a PE-XL Autosystem equipped with an FID detector (carrier=He (constant flow, 2.2 ml/min); mode=split (split ratio=80:1); injector *T*=250 °C; detector (FID) *T*=280 °C).

4.2. Materials and reagents

All organic reagents (purchased from Fluck) were used directly. $Na_2WO_4\cdot 2H_2O$, $NaSiO_4\cdot 9H_2O$, $Al(NO_3)_3$, $Ga(NO_3)_3$, $In(NO_3)_3$, and $Tl(NO_3)_3$ were purchased from Beijing Chemical Reagent Co.

4.3. Catalysts preparation and analysis

$Na_9HSiW_9O_{34}\cdot 13H_2O$ was prepared according to previous method.[23] The synthesis of the catalyst $Na_4H_3[SiW_9Al_3(H_2O)_3O_{37}]\cdot 12H_2O$ polyoxometalate was proceeded according to previous literature[24] and made some redresser: to a stirred solution of 21 g (7.6 mmol) of $Na_9HSiW_9O_{34}\cdot 13H_2O$ in 120 ml hot water (90 °C) was added in small portions 5.7 g (22.7 mmol) of solid $Al(NO_3)_3\cdot 9H_2O$. The pH of the mixture was adjusted to 5 with sodium carbonate and kept at the temperature (90 °C) for 30 min, then cooled, and filtered. Twice its volume of cold methanol was added to the cold filtrate (5 °C). The precipitated white salt was filtered off. The obtained solid was washed with a 2:1 (v/v) methanol/water mixture, and recrystallized three times with warm water (50–60 °C). After filtering, the salt was air-dried. The structure of the powder was confirmed as $Na_4H_3[SiW_9Al_3(H_2O)_3O_{37}]\cdot 12H_2O$ from IR and UV spectroscopic data and elemental analysis (Figs. 1 and 2). Purities of all prepared catalysts were ≥98% according to the analysis.

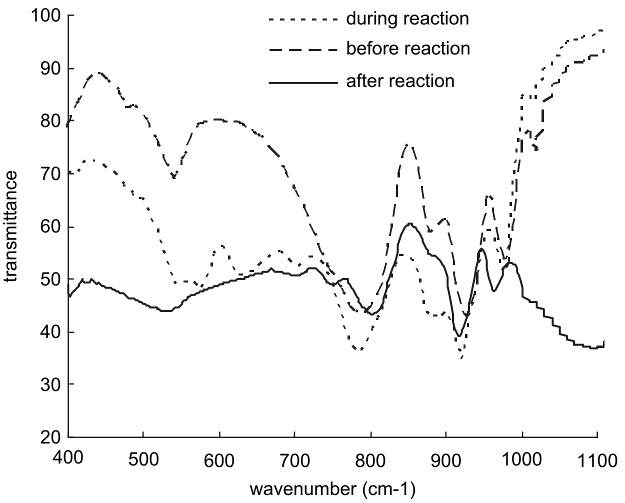


Figure 1. IR spectra of catalyst SiW_9Al_3 before, during, and after reaction.

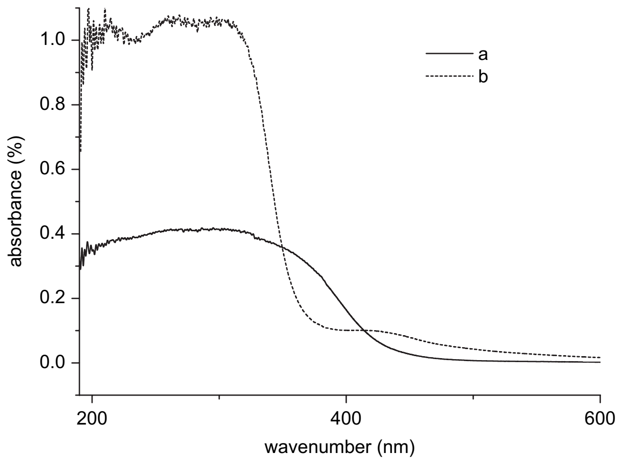


Figure 2. UV–vis spectra of catalyst: (a) before reaction and (b) during reaction.

4.3.1. Data of analysis. Thermogravimetric analysis indicated that there were 15 water molecules per heteropoly compound ($Na_4H_3[SiW_9Al_3(H_2O)_3O_{37}]\cdot 12H_2O$) and the results of elemental analysis in % (w/w) were: Si 1.00 (1.03), W 60.89 (60.84), Al 2.98 (2.98), Na 3.38 (3.37), H 0.10 (0.10), O 21.71 (21.75), H_2O 9.94 (9.92) found (calculated).

4.4. General procedure for oxidation of alcohols

A 25-ml round bottomed flask with 2 ml of CH_3CN (or solvent-free) equipped with a magnetic stirrer and reflux condenser was charged with 0.1 g (1.7 μmol) catalyst and 0.04 mol (2.7 ml) aqueous hydrogen peroxide (30%). The mixture was stirred at desired temperature for 30 min, and then 0.02 mol (2 ml) alcohol was added. The biphasic mixture was stirred at 90 °C for 9 h. After the reaction, the mixture was treated with a 10% sodium hydrogen sulfite solution to decompose the unreacted hydrogen peroxide and then with 10% sodium hydroxide. The product was extracted with *n*-butyl-ether. The pure product was obtained by distillation or silica gel column chromatography (hexane/ethyl acetate, 10–20/1). Spectral data of each product were compared with the literature values.[21,25]

4.5. Procedure for oxidation of cyclohexanol and reusing of the catalyst

A 25-ml round bottomed flask equipped with a magnetic stirrer and reflux condenser was charged with 0.1 g (1.7 μmol) catalyst and 0.04 mol (2.7 ml) aqueous hydrogen peroxide (30%). The mixture was stirred at desired temperature for 30 min, and then 0.02 mol (2 ml) cyclohexanol was added. The mixture was stirred at 90 °C for 9 h. After the reaction, the organic phase was separated, washed with 2 ml $Na_2S_2O_3$, and distilled to gain the product. Spectral data of each product were compared with the literature values.

4.5.1. The 2–5 run. A 25-ml round bottomed flask equipped with a magnetic stirrer and reflux condenser was charged with the aqueous phase of the last run containing the polyoxometalate catalyst 0.1 g (1.7 μmol), distillation residue of the last run containing some polyoxometalate catalyst, and 0.04 mol (2.7 ml) hydrogen peroxide (30%). The mixture was stirred at desired temperature for 30 min, and then 0.02 mol (2 ml) cyclohexanol was added. The biphasic mixture was stirred at 90 °C for 9 h. After the reaction, the organic phase was separated, washed with 2 ml $Na_2S_2O_3$, and distilled to gain the product. Spectral data of each product were compared with the literature values.[25] The catalyst during and after reaction was characterized by IR and UV–vis, and spectroscopic data indicated that the catalyst is stable for the selective oxidation of alcohols (Figs. 1 and 2).

4.5.1.1. Cyclohexanone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65–2.1 (m, 6H), 2.4–2.5 (m, 4H); ^{13}C NMR δ 26.0, 28.1, 42.0, 212.7.

4.5.1.2. Cyclopentanone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75–2.25 (m, 4H), 2.26–2.36 (m, 4H); ^{13}C NMR δ 24.3, 37.6, 217.47.

4.5.1.3. 2-Butanone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02–1.07 (m, 3H), 1.8–2.3 (m, 2H), 2.40–2.49 (m, 3H); ^{13}C NMR δ 7.65, 29.5, 37.2, 210.1.

4.5.1.4. Octan-2-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81–0.89 (m, 3H), 1.15–1.40 (m, 6H), 1.50–1.54 (m, 2H), 2.10 (s, 3H), 2.39 (t, 2H, J=7.4 Hz); ^{13}C NMR δ 14.0 (q), 22.5 (t), 23.9 (t), 29.0 (t), 29.7 (q), 31.7 (t), 43.7 (t), 208.7 (s).

4.5.1.5. *n*-Hexanoic acid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81–0.84 (m, 3H), 1.29–1.7 (m, 6H), 2.31–2.33 (m, 2H), 11.66 (s, 1H); ^{13}C NMR δ 13.79, 22.35, 24.47, 31.34, 34.21, 180.7.

4.5.1.6. Octanoic acid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, J=7.1 Hz), 1.21–1.38 (m, 11H), 1.59–1.67 (m, 2H), 2.32–2.37 (m, 1H), 4.12 (q, 2H, J=7.5 Hz); ^{13}C NMR δ 14.05, 14.24, 22.58, 24.90, 29.05, 29.08, 31.64, 34.38, 176.95.

4.5.1.7. 2-Ethyl-1,3-hexanediol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80–1.05 (m, 6H), 1.4–1.70 (m, 4H), 2.20–2.82 (m, 1H, J=6.5 Hz), 3.68 (2H, d); ^{13}C NMR δ 11.8, 13.8, 16.8, 21.5, 45.2, 55.7, 62.9, 215.2.

4.5.1.8. 1-Hydroxy-2,2,4-trimethyl-3-pentanone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, 6H, J=6.4 Hz), 1.18 (s, 6H), 2.55 (br d, 1H, J=7.4 Hz), 3.25–2.80 (m, 1H), 3.52 (s, 2H); ^{13}C NMR δ 19.8, 21.0, 34.5, 49.6, 69.3, 221.5.

4.5.1.9. 1-Hydroxyoctan-2-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 2H), 3.14 (s, 1H), 2.37 (t, 2H, J=6.9 Hz), 1.61–1.63 (m, 2H), 1.25–1.35 (m, 6H,), 0.85 (t, 3H, J=7.0 Hz); ^{13}C NMR δ 14.1, 22.5, 23.8, 28.9, 31.5, 38.5, 68.2, 210.0.

4.5.1.10. 3-Hydroxymethyl-cyclopentanone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63–1.85 (m, 7H), 2.83 (s, 1H), 3.76 (2H, d, J=6.3 Hz); ^{13}C NMR δ 25.5, 38.0, 38.9, 42.1, 64.9, 220.1.

4.5.1.11. 6-Hydroxy-2-hexanone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30–1.32 (m, 1H), 2.55–1.96 (m, 5H), 3.67 (s, 2H); ^{13}C NMR δ 23.5, 31.3, 42.1, 42.7, 62.1, 211.6.

4.5.1.12. 5-Hydroxy-2-pentanone. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.26–1.28 (m, 1H), 1.66–2.00 (m, 2H), 2.55–2.30 (m, 4H), 3.64 (t, 2H, J=6.3 Hz); ^{13}C NMR δ 26.4, 28.8, 39.4, 61.9, 212.1.

4.5.1.13. 1-Hydroxyoctan-7-one. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.85 (t, 3H, J=6.8 Hz), 1.21–1.38 (m, 6H), 1.61 (m, 2H), 2.37 (t, 2H, J=7.6 Hz), 3.14 (s, 1H), 4.21 (s, 2H); ^{13}C NMR δ 14.1, 22.5, 23.8, 28.9, 31.5, 38.5, 68.2, 210.0.

4.5.1.14. 2-Cyclohexen-1-one. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.36–2.40 (m, 2H), 2.50–2.59 (m, 2H), 6.13 (1H, dt, J=4.2, 2 Hz), 7.45 (1H, dd, J=8.1, 2.8 Hz); ^{13}C NMR δ 22.79, 25.72, 38.13, 129.84, 150.86, 199.65.

4.5.1.15. 3-Octen-2-one. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.90 (t, 3H, J=7.6 Hz), 1.20–1.80 (4H, m), 2.23 (2H, m), 2.30 (s, 3H), 6.00 (d, 1H, J=16.6 Hz), 6.71 (dt, 1H, J=16.5, 7.0 Hz); ^{13}C NMR δ 13.9, 21.88, 27.12, 30.28, 32.17, 132.13, 148.65, 201.14.

4.5.1.16. 11-Dodecen-2-one. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.2–1.40 (m, 10H), 1.50–1.62 (m, 2H), 2.02 (m, 2H), 2.14 (s, 3H), 2.42 (t, 2H, J=6.9 Hz), 4.90–5.02 (m, 2H), 5.80 (tdd, 1H, J=6.8, 10.6, 16.9 Hz); ^{13}C NMR δ 23.8, 29.0, 29.13, 29.26, 29.31, 29.80, 33.75, 43.78, 114.12, 138.76, 210.11.

4.5.1.17. 1-Dodecen-3-one. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.91 (t, 3H, J=7.1 Hz), 1.20–1.40 (m, 12H), 1.50–1.70 (m, 2H), 2.61 (t, 2H, J=7.6 Hz), 5.85 (dd, 1H, J=1.6, 10.9 Hz), 6.20 (dd, 1H, J=1.6, 18.1 Hz), 6.41 (dd, 1H, J=10.9, 19.6 Hz); ^{13}C NMR δ 14.07, 22.63, 24.00, 29.25, 29.40, 31.85, 39.85, 127.81, 136.60, 200.98.

4.5.1.18. Benzaldehyde. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45–7.85 (m, 5H), 10.01 (s, 1H); ^{13}C NMR δ 128.8, 129.5, 134.3, 136.2, 192.2.

4.5.1.19. 4-Methoxybenzaldehyde. ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.86 (s, 3H), 6.95 (d, 2H, J=8.6 Hz), 7.85 (d, 2H, J=8.4 Hz), 10.08 (s, 1H); ^{13}C NMR δ 55.4, 114.1, 129.7, 131.8, 164.4, 190.6.

4.5.1.20. 4-Chlorobenzaldehyde. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71–7.75 (m, 4H), 10.02 (s, 1H); ^{13}C NMR δ 129.2, 130.5, 131.9, 134.7, 190.3.

4.5.1.21. 4-Nitrobenzaldehyde. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, 2H, J=8.1 Hz), 8.3 (d, 2H, J=7.9 Hz), 10.3 (s, 1H); ^{13}C NMR δ 124.2, 130.5, 139.9, 151.0, 190.2.

4.5.1.22. 2-Pyridinecarboxaldehyde. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.5–7.6 (m, 1H), 7.8–8.0 (m, 2H), 8.8–9.0 (m, 1H), 10.1 (s, 1H); ^{13}C NMR δ 193.3, 152.7, 150.2, 137.2, 127.8, 121.9.

4.5.1.23. Furfural. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.6 (s, 1H), 7.4 (s, 1H), 7.8 (s, 1H), 9.7 (s, 1H); ^{13}C NMR δ 112.6, 121.1, 148.1, 153.0, 178.8.

4.5.1.24. 2-Thiophenecarboxaldehyde. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.0–7.3 (m, 1H), 7.6–7.9 (m, 2H), 10.1 (s, 1H); ^{13}C NMR δ 128.6, 135.4, 136.7, 144.1, 183.1.

References and notes

1. (a) Hudlicky, M. *Oxidation in Organic Chemistry*; American Chemical Society: Washington, DC, 1990; (b) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; (c) Luzzio, F. A. *Org. React.* **1998**, *53*, 1–221; (d) Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W.; Pattenden, G.; Moody, C. J. *Comprehensive Organic Functional Group Transformations*; Elsevier Science: Oxford, 1995; Vols. 3 and 5; (e) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977–1986.
2. (a) Arterburn, J. B. *Tetrahedron* **2001**, *57*, 9765–9788; (b) Gogoi, P.; Kumar, G.; Konwar, D. *J. Org. Chem.* **2004**, *69*, 5153–5154; (c) Xi, Z. W.; Zhou, N.; Sun, Y.; Li, K. L. *Science* **2001**, *292*, 1139–1141.
3. Sato, K.; Aokil, M.; Noyori, R. *Science* **1998**, *281*, 1646–1647.
4. Deng, Y. Q.; Ma, Z. F.; Wang, K.; Chen, J. *Green Chem.* **1999**, *1*, 275–276.
5. Guo, M. L. *Chin. J. Catal.* **2003**, *24*, 483–484.
6. Indira, V.; Joy, P. A.; Gopinathan, S. C.; Gopinathan. *Indian J. Chem. Sect. A* **1998**, *37*, 261–267.
7. Wei, J. F.; Shi, X. Y.; He, D. P.; Zhang, M. *Chin. Sci. Bull.* **2002**, *47*, 1628–1630.
8. Sato, K.; Aokil, M.; Takagi, J.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 12386–12387.
9. Manyar, H. G.; Chaure, G. S.; Kaman, A. *Green Chem.* **2006**, *4*, 344–346.
10. Zhou, M. J.; Wei, Ch. P.; Bi, Y. L.; Zhen, K. J. *Chin. J. Catal.* **1999**, *20*, 437–441.
11. Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536–538.
12. Loose, I.; Bösing, M.; Klein, R.; Krebs, B.; Schulz, R. P.; Scharbert, B. *Inorg. Chim. Acta* **1997**, *263*, 99–108.
13. Hill, C. L.; Zhang, X. *Nature* **1995**, *373*, 324–325.
14. Zhang, X.; Sasaki, K.; Hill, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 4809–4816.
15. Neumann, R.; Abu-Gnim, C. *J. Am. Chem. Soc.* **1990**, *112*, 6025–6031.
16. Khenkin, A. M.; Hill, C. L. *Mendeleev Commun.* **1993**, 140–141.
17. Neumann, R.; Gara, M. *J. Am. Chem. Soc.* **1994**, *116*, 5509–5510.
18. Gara, M. *J. Am. Chem. Soc.* **1995**, *117*, 5066–5074.
19. Wang, J.; Yan, L.; Li, G.; Wang, X.; Ding, Y.; Suo, J. *Tetrahedron Lett.* **2005**, *46*, 7023–7027.
20. (a) Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587–3593; (b) Ventuello, C.; Alneri, E.; Ricci, M. *J. Org. Chem.* **1983**, *48*, 3831–3833; (c) Bortolini, O.; Furia, F. D.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688–2690.
21. Bogdal, D.; Łukasiewicz, M. *Synlett* **2000**, 143–145.
22. Trost, B. M.; Masuyama, Y. *Tetrahedron Lett.* **1984**, *25*, 173–176.
23. Herve, G.; Teze, A. *Inorg. Chem.* **1977**, *16*, 2115–2117.
24. Liu, J. F.; Meng, L.; Zhao, B. L. *Chem. J. Chin. Univ.* **1993**, *14*, 602–604.
25. (a) Simoms, W. W.; Zanger, M. *The Sadtler Guide to NMR Spectra*; Sadtler Research Laboratories: Philadelphia, PA, 1972; (b) Pouchert, C. J.; Campbell, J. R. *The Aldrich*

Library of NMR Spectra; Aldrich Chemical: Milwaukee, Wisconsin, WI, 1974; (c) Dzhemilev, U. M.; Khusnutdinov, R. I.; Atnabaeva, A. M.; Muslimov, Z. S.; Parfenova, R. I.; Tomilov, Yu. V. *Russ. Chem. Bull.* **2001**, *50*, 1242–1247; (d) Kuhakarn, C.; Kittigowittana, K.; Pohmakotr, M.; Reutrakul, V. *Tetrahedron* **2005**, *61*, 8995–9000; (e) Muzart, J.; Pale, P.; Pete, J.-P. *J. Organomet. Chem.* **1988**, *353*, 267–273; (f) Kourouli, T.; Kefalas, P.; Ragoussis, N.; Ragoussis, V. *J. Org. Chem.* **2002**, *67*, 4615–4618; (g) Sinha, S. C.; Sinha-Bagchi, A.; Keinan, Eh. *J. Org. Chem.* **1993**, *58*, 7789–7796; (h) Kitamura, M.; Lee, D.; Hayashi, S.; Tanaka, S.; Yoshimura, M. *J. Org. Chem.* **2002**, *67*, 8685–8687; (i) Sekiyama, Y.; Fujimoto, Y.; Hasumi, K.; Endo, A. *J. Org. Chem.* **2001**, *66*, 5649–5654; (j) Pyun, S. Y.; Lee, D. C.; Seung, Y. J.; Cho, B. R. *J. Org. Chem.* **2005**, *70*, 5327–5330; (k) Plietker, B. *J. Org. Chem.* **2004**, *69*, 8287–8296; (l) Sato, K.; Aoki, M.; Takagi, J.; Zimmermann, K.; Noyori, R. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2287–2306.