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$AlCl_3$-catalyzed oxidation of alcohol

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ABSTRACT

The metalloid salt $AlCl_3$, applied as catalyst for the oxidation of alcohol was presented. In water media, variety of alcohols, including inactive aliphatic alcohols, could be converted into corresponding carbonyl compounds with excellent conversion and selectivity. Especially, this green reaction system also exemplifies advances toward the domino synthesis alkenes in good yields (>52%) and perfect purity (>99%), and the reaction gave preferentially the *E*-isomer. The obvious advantages of the present protocol include green reaction media, wide functional group tolerance, convenient product isolation, as well as grams reaction scale.

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1. Introduction

Indubitably, oxidation of alcohols to their corresponding carbonyl compounds is one of the most important and challenging transformations in the synthesis of fine chemicals and intermediates.[1] Traditional methods always use large amounts of transition-metal involved noxious oxidants, such as chromate and permanganate,[2] or non-green organic solvents,[3] or require severe reaction conditions.[4]

From an environmental and economic viewpoint, these procedures are discouraged for the reason that most of them suffer from low atom efficiency[5] and a large amount of waste products,[6] leading to a severe environmental impact.[7] Consequently, the extensive research interests focused on metal-catalyzed oxidation systems, which prefer to use molecular oxygen as the terminal oxidant since innocuous byproducts (H_2O or H_2O_2) and high atom economy.[8,9] Transition-metal-catalyzed aerobic oxidation of alcohols has recently been reviewed,[10] and these reviews outline significant progress in the elaboration of homogeneous and/or heterogeneous catalysts in general. However, for the most cases, harmful organic solvents are always indispensable,[11] such as *N*-hydroxyphthalimide,[12] diethyl azodicarboxylate,[13] or nitrasonium ions,[14] and some ligands[15] were required to accomplish the catalytic cycle, as well as the catalyst separation and recycling of homogeneous metal catalysts[16] often make practical and industrial applications very difficult. Among them, the monomerically (or highly) dispersed metal hydroxide species on the appropriate supporters turned out to be a powerful heterogeneous catalyst for the alcohol oxidation. For the representative work as example, Al_2O_3 supported Ru^{IV}–OH catalyst.[17] The noble-metal mediated catalyst system demonstrated high turn over numbers (up to 980), effective reusable property and wide functional group tolerance. Even though the excellent catalytic performance, the limitations for the adsorbed type catalyst system are obvious, such as catalyst leaching, using of harmful solvent and more complicated synthesis procedure.

We considered that the most preferable oxidation procedures were that the oxidation reactions could be carried out in harmfulness solvent, the system would facilitate the separation of products and even to prevent use of expensive catalyst. In the ongoing research programs, we found that in water media, Lewis acid, $AlCl_3$, plays dominant role in the oxidation of alcohols in the presence of Oxone®. This novel oxidation system could convert variety of alcohols to the corresponding carbonyl compounds. Evidently, $AlCl_3$ hydrolyzed to oligomers $[Al_2(OH)_nCl_{6-n}]_m$ in aqueous phase firstly, the hydrolyzed products have been regarded as water-soluble supporter, the in situ formed Al–OH was possibly applied as key intermediate for alcohol oxidation. Then our much attention were attracted by the metalloid elements, such as Al, Si, involved substances because that the structurally common units Al–OH, Si–OH are extensively exist in such materials, for example, polygorskite, silica gel, and organosilicon. The screening experiments were tested,

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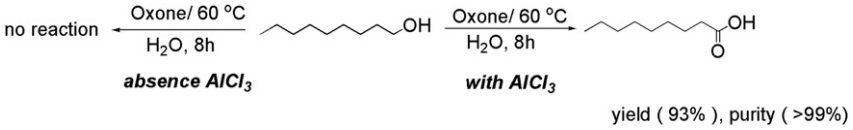
under specific conditions, polygorskite, silica gel, and organosilicon demonstrated average to excellent catalytic behavior for the oxidation of alcohols. Due to the pioneering work, it is convinced that in the transition-metal catalyst dominated field of alcohol oxidation, the metalloid elements Al and Si will be important members in the future. Our preliminary study disclosed that the efficient, environmentally friendly, and inexpensive catalyst system, which renders the oxidation of alcohols with advantages, such as green reaction media, mild reaction conditions, wide functional group tolerance, and convenient product isolation, as well as grams reaction scale. In this communication, we report $AlCl_3$ catalyzed oxidation of alcohols in the presence of Oxone® in water media, furthermore, its application in the domino synthesis of *E*-isomer alkene by alcohol oxidation and Wittig reaction was also studied.

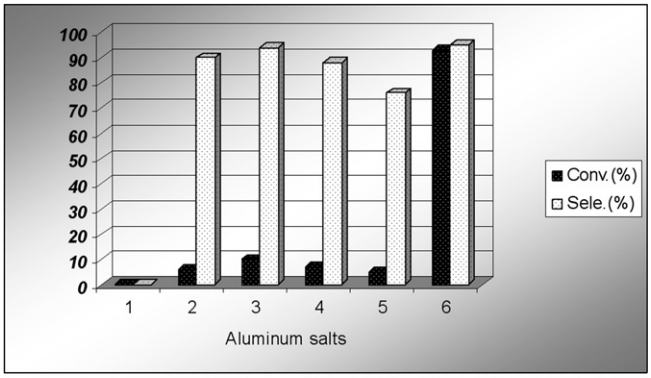
2. Results and discussion

2.1. Catalytic activity in *n*-nonyl alcohol

In order to study the catalytic activity of $AlCl_3$, the oxidation of *n*-nonyl alcohol was determined as the model reaction to screen the influence factors, such as the temperature, the amount of the catalyst, and Oxone®, as well as the reaction time. The appropriate condition is optimized as *n*-nonyl alcohol (0.1 mmol), Oxone® (2.4 equiv), and the ratio of alcohol to $AlCl_3$ is 0.1/0.27, stirred in water at 60 °C for 8 h, the reaction afforded nonanoic acid, which was isolated in 93% yield and excellent purity (>99%). In a controlled experiment, in the absence of $AlCl_3$ or under entirely uniform pH conditions without $AlCl_3$, it was found that the reaction did not proceed even after a longer reaction time (Scheme 1). In the presence of other aluminum salts and other metal chlorides, such as $Al(OH)_3$, Al_2O_3, $MgCl_2\cdot 6H_2O$, and $SnCl_2\cdot 2H_2O$, which gave poor conversion (Fig. 1). Notably, under the specific reaction conditions, only $AlCl_3$ involved oxidation system gave product with excellent conversion and selectivity.



Scheme 1. The controlled experiment.



1, without aluminum salt; 2, $Al(OH)_3$; 3, γ- Al_2O_3; 4, $MgCl_2 \cdot 6H_2O$; 5, $SnCl_2 \cdot 2H_2O$; 6, $AlCl_3$

Fig. 1. The oxidation of *n*-nonyl alcohol in the presence of other aluminum salts.

2.2. Oxidation of a series alcohols

To evaluate the scope of Al-involved catalytic system, we investigated the oxidation of a number of alcohols (Table 1). Benzyl alcohols were oxidized to the corresponding acids with 100% conversion at room temperature (entries 1–3). And the reaction also provided good-to-excellent yields and purities (>99%) in the oxidation of benzhydrol (**1d**) and substituted benzhydrols, such as 4-methylbenzhydrol (**1e**) and 4-chlorobenzhydrol (**1f**) (entries 4–6). Cyclopentanol (**1g**) and cyclohexanol (**1h**) were transformed to the respective ketone in high isolated yields and perfect purity (>99%) (entries 7–8). Surprisingly, aliphatic alcohols, which are inactive in most oxidation systems, were performed excellent activity. *n*-Hexyl alcohol (**1i**), *n*-octanol (**1j**), and *n*-nonyl alcohol (**1k**) were all converted to the corresponding acid with 100% conversion and selectivity, respectively (entries 9–11). However, with the increasing of the number of carbon atoms, the conversions were reduced from 70% to 26%, even the temperature was elevated to 60 °C (entries 12–14).

So as to apply the system to industrial research, several representative oxidation alcohols were tested in more large scale (Scheme 2). The typical experimental process as follows: Oxone® (2.4 equiv) and the relevant $AlCl_3$ were added to a solution of alcohol (10 g) in water. After stirring at rt/60 °C for 4–8 h, the product was precipitated on the reactor vessel with excellent yields (>93%), especially, most crude product's NMR purity was up to 99%.

2.3. The domino synthesis of alkene in the system

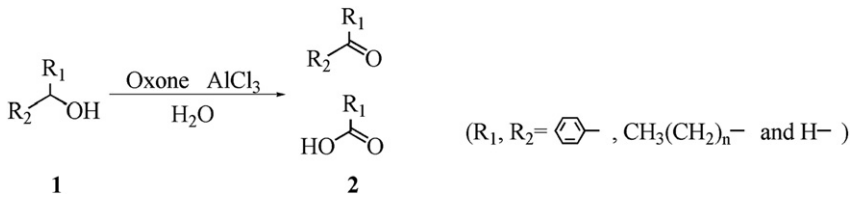
Wittig reaction has excelled as one of the most popular and powerful methods to create carbon–carbon double bonds in synthetic chemical methodology. The use of ylides in the presence of aldehydes to provide access to alkenes with either high *E*- or *Z*-geometrical selectivity has been researched extensively over many years.[18,19] In order to extend the application of our clean reaction system, the domino synthesis of alkenes, started from oxidation and then olefination, has been studied. Under the optimized conditions, after adding ylides, the final product of alkene was obtained only. The oxidation of in situ generated aldehyde was diminished (Scheme 3). Then we broaded the scope of domino synthesis alkene, and the representative procedure carried out as follows. The required amount of Oxone® (2.4 equiv), ylides (1.5 equiv), and the relevant $AlCl_3$ were added to a solution of the alcohol (2 mmol) in water. Then, the mixture was stirred at rt for 2–4 h. The result suggested that our catalysis system provided complete bias to olefination compounds (Table 2).

We examined the scope of the aqueous Wittig reaction for the synthesis of alkene. The results are depicted in Table 2. The Wittig reaction in water is a straightforward protocol that works favorably between yields and aromatic alcohols having electron donating or electron withdrawing groups. All the products were isolated in moderate to excellent yields and the reaction gave preferentially the *E*-isomer. The presence of electron withdrawing groups increased the reaction rates (entries 2–4), whereas electron-releasing groups gave the corresponding product in lower yield (entries 5–9).

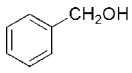
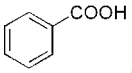
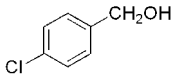
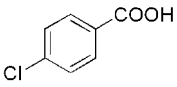
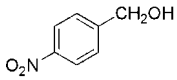
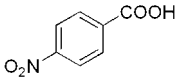
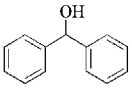
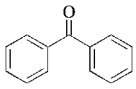
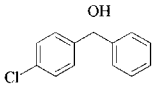
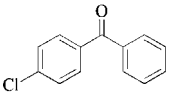
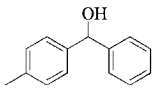
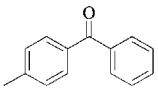
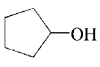
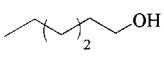
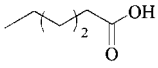
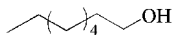
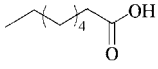
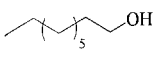
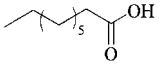
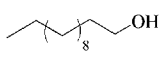
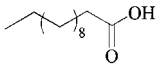
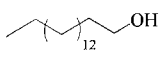
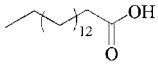
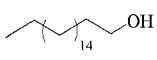
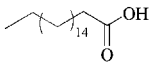
2.4. Discussion of the reaction mechanism

Based on the literatures,[17,20–22] we have proposed a plausible mechanism for the alcohol oxidation (Scheme 4), that proceeds via an aluminium alkoxide intermediate **II**, which was formed between

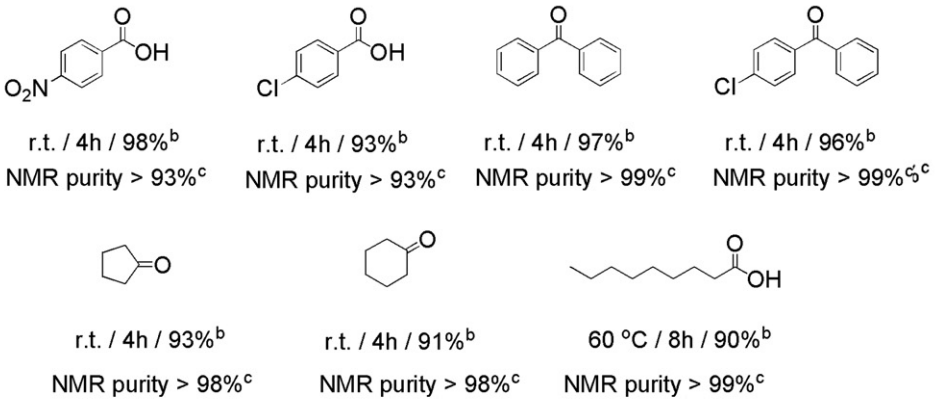
Table 1
Oxidation of a series of alcohols[a]



1 2

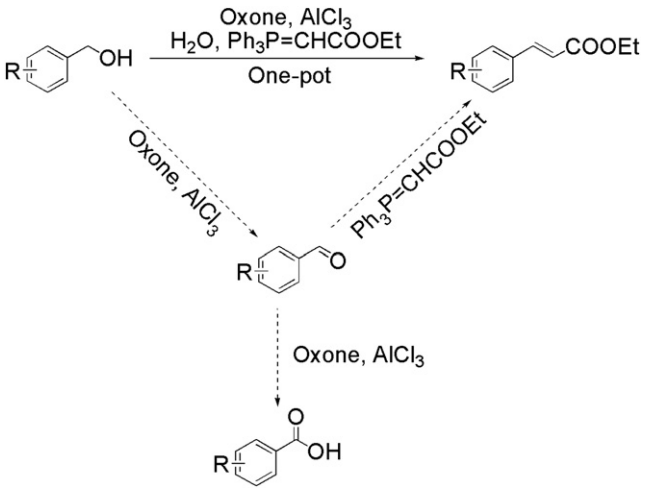
Entry	Substrate	Product	T (°C)	t (h)	Conv. (%)	Sele. (%)	Yield[b] (%)
1	 1a	 2a	rt	4	100	83	80
2	 1b	 2b	rt	4	100	80	77
3	 1c	 2c	rt	4	87	92	76
4	 1d	 2d	rt	4	100	100	98
5	 1e	 2e	rt	4	100	100	97
6	 1f	 2f	rt	4	100	100	96
7	 1g	 2g	rt	4	100	100	90
8	 1h	 2h	rt	4	100	100	93
9	 1i	 2i	60	8	100	100	88
10	 1j	 2j	60	8	100	100	91
11	 1k	 2k	60	8	100	100	93
12	 1l	 2l	60	8	70	100	52
13	 1m	 2m	60	8	54	100	36
14	 1n	 2n	60	8	26	73	nr

[a] Reaction condition: alcohol 0.10 mmol, $AlCl_3$ 2.7 equiv, Oxone®/alcohol=2.4:1, water 3 mL. Percentage conversation and reaction selectivity were determined by GC analysis.
[b] Yield of isolated product.



[a] Reaction condition: The required amount of Oxone® (2.4 equiv.) and the relevant $AlCl_3$ were added to a solution of the alcohol (10 g) in water.
[b] Isolated Yield.
[c] Crude product's NMR purity.

Scheme 2. Oxidation of representative alcohols in grams scale.[a]



Scheme 3. The competitive reaction between oxidation and olefination.

alcohol and hydrolyzed $AlCl_3$ **I**, and then **II** undergoes β-hydrogen elimination to produce the carbonyl compound and aluminium hydride species **III**. As reported that in the presence of Oxone®, free ion Cl^- could be generated to the more effective oxidizing agent Cl^+,[21] which possibly chloridize aluminium hydride species to the intermediate Al—Cl **IV**, in the following step, hydrolyzation of Al—Cl occurred and the hydrolysate Al—OH regarded as catalytic species, started the next catalytic cycle.

In order to determine the plausible mechanism, isotope-labeled alcohols were performed in the presence of $AlCl_3$/Oxone®/H_2O under N_2 sphere (Scheme 5), GC/MS detector indicated that the abundance of ^{16}O in product was >97%. That is, the dehydration process involving a selective cleavage of the C—O bond of the alcohol with concomitant formation of a new C=O bond, in the product, the oxygen atoms transfer from Oxone or solvent. The further study demonstrated that when the oxidation of isotope-labeled alcohols was carried out in the solvent of $H_2{}^{18}O$, the abundance of ^{18}O in product surprisingly increased to 90%. This interesting finding verified that in the process of oxidation alcohol, the exchange of oxygen atoms between alcohol and water was taken placed. Another 10% amount of ^{16}O labeled product probably originates from the hydrolyzation of species IV with $H_2{}^{16}O$.

3. Conclusions

In conclusion, we have developed a green, clean, and highly active catalytic system for the oxidation of a wide variety of alcohols, including benzyl alcohols, benzhydrols, cyclic, and aliphatic alcohols. Especially, this green reaction system also exemplifies advances toward the domino synthesis alkene in good yields (>52%) and perfect purity (>99%), and the reaction gave preferentially the *E*-isomer. Remarkably, this new form of oxidation reaction is interesting in keeping with the notion of green chemistry due to non-use of heavy metals and halogenated solvents, less waste reducts, high-yielding (even in large scale), mild conditions, easy to work up (most do not require chromatography) and should provide a mild oxidative alternative for organic chemists.

4. Experimental

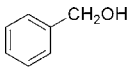
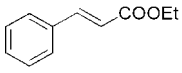
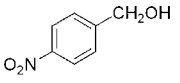
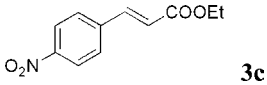
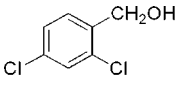
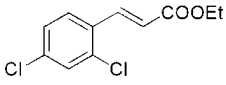
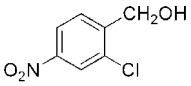
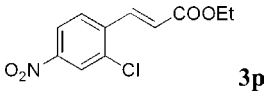
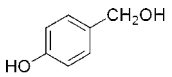
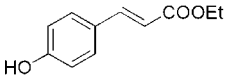
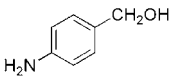
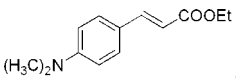
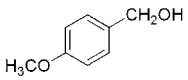
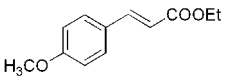
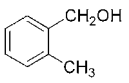
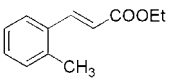
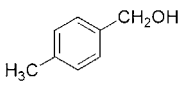
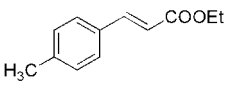
4.1. General remarks

Oxone® was obtained from commercial sources. All solvents used were analytical grade and were used as received. All of the alcohols used in the reaction were obtained from ABCR GmbH & Co. KG. and used without further treatment. $H_2{}^{18}O$ was obtained from Huayi Isotope Co. and used as received. The melting points of isolated products were determined on a WRS-1A digital melting point apparatus. All NMR spectra are recorded on MERCURY (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR) spectrometers; chemical shifts are expressed in parts per million (δ units) relative to TMS signal as an internal reference in $CDCl_3$ or DMSO-d_6. Gas chromatography (GC) analysis was performed on a Shimadezu GC-2010 equipped with a 15 m×0.53 mm×1.5 μm RTX-1 capillary column and a oxyhydrogen flame detector. GC/MS analysis were carried out on a trace HP GC6890/MS5973 equipped with a 25 m×0.25 mm SE-54 column and a Shimadzu GC-16A gas chromatograph with a 3 m×3 mm OV-17 column.

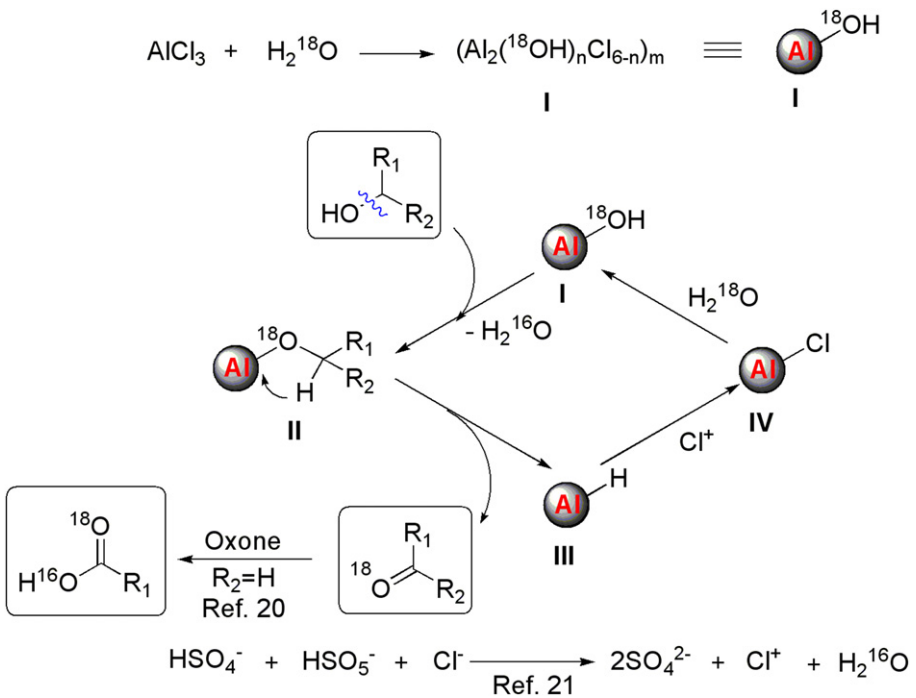
4.2. General procedure for the oxidation of alcohol

A typical reaction was carried out as follows: *n*-nonyl alcohol (0.1 mmol), Oxone® (2.4 equiv), and $AlCl_3$ (2.7 equiv) were dissolved in 3 mL of water. The mixture was stirred at 60 °C for 8 h and monitored by TLC. After completion, it was extracted with ethyl

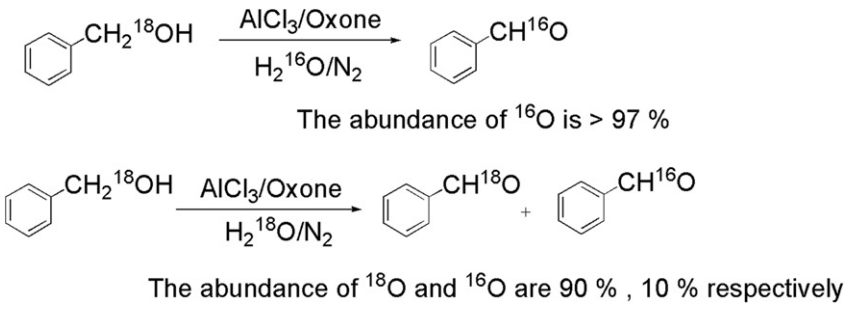
Table 2
The domino synthesis of alkene[a]

Entry	Substrate	Product	*t* (h)	Yield[b] (%)
1	 **1a**	 **3a**	2	68
2	 **1c**	 **3c**	2	75
3	 **1o**	 **3o**	2	80
4	 **1p**	 **3p**	2	93
5	 **1q**	 **3q**	3	56
6	 **1r**	 **3r**	3	58
7	 **1s**	 **3s**	3	55
8	 **1t**	 **3t**	4	52
9	 **1u**	 **3u**	3	60

[a] Reaction condition: the required amount of Oxone® (2.4 equiv), ylides (1.5 equiv), and the relevant $AlCl_3$ were added to a solution of the alcohol (2 mmol) in water, room temperature.
[b] Yield of isolated product.



Scheme 4. The plausible reaction mechanism.



Scheme 5. The oxidation of isotope-labeled alcohols.

acetate. The organic layer was dried and removed under reduced pressure to give the desired crude product. Analytically pure products were obtained after recrystallizing or column chromatography using petroleum ether and ethyl acetate (10:1, v/v) as eluent. Formation of products and consumption of substrates were monitored by GC. The identity of products was determined either by comparison with authentic samples using gas chromatography or by NMR analysis. The conversion and product selectivity were determined using GC analysis.

4.3. General procedure of large scale for isolating products

The required amount of Oxone® (2.4 equiv) and the relevant $AlCl_3$ were added to a solution of the alcohol (10 g) in water. Then, the mixture was stirred at 60 °C/rt for 4–8 h and monitored by TLC. After completion, the suspension was filtrated and the solution was extracted with ethyl acetate. The organic layer was removed under reduced pressure to give the desired crude products. The solid and crude products were washed by petroleum ether several times to obtain the analytically pure products. Formation of products and consumption of substrates were monitored by GC. The identity of products was determined either by comparison with authentic samples using gas chromatography or by NMR analysis. The conversion and selectivity were determined using GC analysis.

4.4. General procedure of the olefination products

The required amount of Oxone® (2.4 equiv), ylides (1.5 equiv), and the relevant $AlCl_3$ was added to a solution of the alcohol (2 mmol) in water, and $AlCl_3$ was added stepwise. Then, the mixture was stirred at rt for 2–4 h, after completion, it was extracted with ethyl acetate. The organic layer was dried and removed under reduced pressure to give the desired crude product. Analytically pure products were obtained after column chromatography using petroleum ether and ethyl acetate as eluent. The identity of products was determined by NMR analysis.

4.5. Preparation of ^{18}O enriched benzyl alcohol

Na (0.05 g) was added to 0.75 mL ^{18}O enriched water (98% $H_2{}^{18}O$, Huayi Isotope Co.) in a flask, and then 0.5 mL 1-chloromethyl benzene was added into the flask. The mixture was heated to 95 °C and refluxed for 48 h with continuous stirring. The product was purified by column chromatography and 0.2 g $C_6H_5CH_2{}^{18}OH$ was obtained. The ^{18}O enriched benzyl alcohol was examined by GC/MS, and the abundance of $C_6H_5CH_2{}^{18}OH$ was 98%.

4.6. Analysis

*4.6.1. The NMR data for the oxidation products **2a**–**g**, **k**.*

*4.6.1.1. Benzyl acid (**2a**).* White solid (0.219 g, 80%); mp=121–122 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=12.35 (s, 1H, COOH), 8.14–8.12 (d, J=8 Hz, 2H, Ar–H), 7.64–7.60 (t, J=8 Hz, 1H, Ar–H), 7.50–7.46 (t, J=8 Hz, 2H, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=172.39, 133.81, 130.20, 129.30, 128.46.

*4.6.1.2. 4-Chlorobenzyl acid (**2b**).* White solid (0.263 g, 77%); mp=201–202 °C; ^1H NMR (400 MHz, DMSO-d_6): δ=13.18 (s, 1H, COOH), 7.96–7.94 (d, J=8 Hz, 2H, Ar–H), 7.58–7.56 (d, J=8 Hz, 2H, Ar–H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.38, 137.76, 131.10, 129.59, 128.70.

*4.6.1.3. 4-Nitrobenzyl acid (**2c**).* Pale-yellow solid (0.2735 g, 76%); mp=241–243 °C; ^1H NMR (400 MHz, DMSO-d_6): δ=13.67 (s, 1H, COOH), 8.34–8.32 (d, J=8 Hz, 2H, Ar–H), 8.19–8.17 (d, J=8 Hz, 2H, Ar–H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=165.73, 150.00, 136.31, 130.64, 123.68.

*4.6.1.4. Benzophenone (**2d**).* White solid (0.3572 g, 98%); mp=46–48 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=7.81–7.80 (m, 4H, Ar–H), 7.60–7.57 (m, 2H, Ar–H), 7.50–7.46 (m, 4H, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.67, 137.57, 132.36, 130.01, 128.23.

*4.6.1.5. 4-Chlorobenzophenone (**2e**).* White solid (0.42 g, 97%); mp=75–79 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=7.79–7.75 (m, 4H, Ar–H), 7.62–7.58 (m, 1H, Ar–H), 7.51–7.46 (m, 4H, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=195.45, 138.88, 137.23, 135.86, 132.60, 131.43, 129.91, 128.61, 128.38.

*4.6.1.6. 4-Methylbenzophenone (**2f**).* White solid (0.3759 g, 96%); mp=55–58 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=7.79–7.77 (d, J=8 Hz, 2H, Ar–H), 7.73–7.71 (d, J=8 Hz, 2H, Ar–H), 7.59–7.55 (t, J=8 Hz, 1H, Ar–H), 7.49–7.45 (t, J=8 Hz, 2H, Ar–H), 7.29–7.27 (t, J=8 Hz, 2H, Ar–H), 2.44 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.43, 143.19, 137.93, 134.87, 132.11, 130.26, 129.88, 128.94, 128.16, 21.63.

*4.6.1.7. Cyclopentanone (**2g**).* Colorless liquid (0.152 g, 90%); ^1H NMR (400 MHz, $CDCl_3$): δ=1.88 (s, 4H, CH_2), 1.71 (s, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ=219.57, 37.60, 22.59.

*4.6.1.8. Nonanoic acid (**2k**).* Colorless oil (0.162 g, 93%); ^1H NMR (400 MHz, $CDCl_3$): δ=11.60 (s, 1H, COOH), 2.37–2.33 (t, J=8 Hz, 2H, CH_2), 1.67–1.63 (t, J=8 Hz, 2H, CH_2), 1.30 (s, 10H, CH_2), 0.90–0.86 (t, J=8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=180.70, 34.13, 31.78, 29.19, 29.04, 24.63, 22.62, 14.04.

*4.6.2. The NMR data for the olefination products **3a**, **3c**, **3o**–**u**.*

*4.6.2.1. (E)-Ethyl cinnamate (**3a**).* Pale-yellow oil (0.2441g, 68%); ^1H NMR (400 MHz, $CDCl_3$): δ=7.60–7.56 (d, J=16 Hz, 1H, CH=), 7.41–7.39 (m, 2H, Ar–H), 7.27–7.26 (m, 3H, Ar–H), 6.35–6.31 (d, J=16 Hz, 1H, CH=), 4.18–4.13 (m, 2H, CH_2), 1.24–1.21 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.76, 144.37, 134.27, 130.03, 128.69, 127.87, 118.09, 60.30, 14.16.

*4.6.2.2. (E)-Ethyl 3-(4-nitrophenyl)acrylate (**3c**).* Pale-yellow solid (0.3316g, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.22–8.20 (d, J=8 Hz, 2H, Ar–H), 7.68–7.66 (d, J=8 Hz, 2H, Ar–H), 7.03–7.00 (d, J=12 Hz, 1H, CH=), 6.15–6.12 (d, J=12 Hz, 1H, CH=), 4.20–4.15 (m, 2H, CH_2), 1.26–1.23 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.29, 141.56, 141.46, 140.48, 130.16, 128.58, 123.15, 60.71, 14.02.

*4.6.2.3. (E)-Ethyl 3-(2, 4-dichlorophenyl)acrylate (**3o**).* White solid (0.3920g, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.03–7.99 (d, J=16 Hz, 1H, CH=), 7.56–7.54 (d, J=8 Hz, 1H, Ar–H), 7.44 (s, 1H, Ar–H), 7.28–7.26 (d, J=8 Hz, 1H, Ar–H), 6.43–6.39 (d, J=16 Hz, 1H, CH=), 4.31–4.24 (m, 2H, CH_2), 1.36–1.33 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.24, 139.11, 136.25, 135.45, 131.31, 129.94, 128.30, 127.52, 121.31, 60.79, 14.28.

*4.6.2.4. (E)-Ethyl 3-(2-chloro-4-nitro phenyl)acrylate (**3p**).* White solid (0.4751g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.385 (s, 1H, Ar–H), 8.14–8.12 (d, J=8 Hz, 1H, Ar–H), 7.57–7.55 (d, J=8 Hz, 1H, Ar–H), 7.10–7.07 (d, J=12 Hz, 1H, CH=), 6.24–6.21 (d, J=12 Hz, 1H, CH=), 4.17–4.12 (m, 2H, CH_2), 1.22–1.19 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.79, 139.81, 138.12, 135.36, 129.90, 126.02, 124.34, 124.07, 122.50, 60.78, 14.22.

*4.6.2.5. (E)-Ethyl 3-(4-hydroxyphenyl)acrylate (**3q**).* White solid (0.2150g, 56%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.66–7.62 (d, J=16 Hz, 1H, CH=), 7.42–7.40 (d, J=8 Hz, 2H, Ar–H), 6.88–6.86 (d, J=8 Hz, 2H, Ar–H), 6.31–6.27 (d, J=16 Hz, 1H, CH=), 4.30–4.24 (m, 2H, CH_2), 1.35–1.32 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.12, 158.22, 144.92, 130.03, 126.80, 115.90, 60.69, 14.26.

*4.6.2.6. (E)-Ethyl 3-(4-(dimethylamino)phenyl)acrylate (**3r**).* Pale-yellow solid (0.2539g, 58%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.64–7.60 (d, J=16 Hz, 1H, CH=), 7.42–7.40 (d, J=8 Hz, 2H, Ar–H), 6.67–6.65 (d, J=8 Hz, 2H, Ar–H), 6.24–6.20 (d, J=16 Hz, 1H, CH=), 4.26–4.21 (m, 2H, CH_2), 3.01 (s, 6H, $N(CH_3)_2$), 1.34–1.31 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.10, 151.93, 145.34, 129.91, 122.51, 112.83, 112.03, 60.25, 40.35, 14.64.

*4.6.2.7. (E)-Ethyl 3-(4-methoxyphenyl)acrylate (**3s**).* Colorless oil (0.2262 g, 55%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.66–7.62 (d, J=16 Hz, 1H, CH=), 7.48–7.46 (d, J=8 Hz, 2H, Ar–H), 6.90–6.88 (d, J=8 Hz, 2H, Ar–H), 6.32–6.28 (d, J=16 Hz, 1H, CH=), 4.27–4.22 (m, 2H, CH_2), 3.83 (s, 3H, $-OCH_3$), 1.34–1.31 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.30, 161.28, 144.23, 129.64, 127.15, 115.67, 114.26, 60.28, 55.37, 14.33.

*4.6.2.8. (E)-Ethyl 3-o-tolylacrylate (**3t**).* White oil (0.1976 g, 52%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.93–7.89 (d, J=16 Hz, 1H, CH=), 7.48–7.46 (d, J=8 Hz, 2H, Ar–H), 7.20–7.11 (m, 3H, Ar–H), 6.31–6.27 (d, J=16 Hz, 1H, CH=), 4.23–4.18 (m, 2H, CH_2), 2.36 (s, 1H, Ar–CH_3), 1.29–1.26 (t, J=12 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.77, 142.04, 137.37, 133.26, 130.58, 129.73, 126.22, 119.15, 60.22, 19.54, 14.16.

*4.6.2.9. (E)-Ethyl 3-p-tolylacrylate (**3u**).* White oil (0.228 g, 60%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.58–7.54 (d, J=16 Hz, 1H, CH=), 7.32–7.30 (d, J=8 Hz, 2H, Ar–H), 7.08–7.06 (d, J=8 Hz, 2H, Ar–H), 6.31–6.27 (d, J=16 Hz, 1H, CH=), 4.18–4.13 (m, 2H, CH_2), 2.26 (s, 3H, Ar–CH_3), 1.25–1.21 (t, J=16 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.01, 144.34, 140.45, 131.63, 129.43, 127.98, 117.18, 60.24, 21.24, 14.25.

Acknowledgements

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