Electronic Supplementary Information (ESI)

Aerobic oxidation and oxidative esterification of alcohols through cooperative catalysis under metal-free conditions

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Experimental Section

Typical procedure for the preparation of PMO-IL

A clear homogeneous solution of Pluronic P123 (1.67 g) and KCl (8.8 g) in distilled water (10.5 g) and HCl (2 M, 46.14 g) was obtained by stirring the mixture at 40 °C. Then, an homogeneous mixture of ionic liquid 1,3-bis(trimethoxysilylpropyl) imidazolium chloride (2 mmol, 0.86 g) and tetramethoxysilane (18 mmol, 2.74 g) in super-dry methanol previously prepared was rapidly added to the above solution kept at 40 °C and stirred for 24 h. The solid material obtained was first dried at 100 °C for 72 h, and then exntesively washed with deionized water, after which it was left to dry at room temperature. Removal of residual surfactant was achieved by stirring the material and ethanol (100 mL) added with concentrated HCl (37%, 3 mL) in a Soxhlet for 24 h.





Typical procedure for the preparation of ABNO@PMO-IL

A Si alkoxide precursor bearing the ABNO was synthesized through reductive ammination of 3-aminopropyl-trimethoxy silane (1 mmol) with keto-ABNO (1 mmol) in the persence of NaBH₃CN (1.1 mmol) by stirring the resulting mixture for 24 h at room tempature in dried MeOH (20 mL) under argon atmosphere. After quenching the excess cyanoborohydride with aqeous HCl (4.0 M, 0.75 mL), the solution containing of percusor was mixed with 1 g of PMO-IL-Cl previously synthesized suspended in dry toluene. The resulting suspension was left under reflux for 36 h under an Ar atmosphere, after which the solid material was filtered and washed extensively with toluene, methanol and ethanol in order to remove any unreacted precusor. The material was then dried in oven at 80 °C to give the ABNO@PMO-IL-Cl at a loading of 0.26 mmol g⁻¹ as determined by thermogravimetric analysis and CHN analysis.



ABNO@PMO-IL-Br

General procedure for oxidation of alcohols using ABNO@PMO-IL-Br

A mixture of substrate (1 mmol), TBN (8 mol%), HCl (10 mol%) and catalyst (1–1.5 mol%) in toluene (0.3 mL) in a flask was charged with pure oxygen (balloon filled, 1 atmosphere O₂). The resulting mixture was stirred at 50 °C for the time indicated in Table 3. Progress of the reaction was monitored by GC. After completion of the reaction, the solution was diluted with ethylacetate and the catalyst was separated by centrifugation. The resulting solution was then dried with sodium sulfate and the excess solvent was removed under reduced pressure to give the corresponding carbonyl compound. The purity of the product each time was analyzed by GC without any chromatographic purification.

General procedure for one-pot oxidative esterification of primary alcohols using ABNO@PMO-IL-Br

A mixture of substrate (1 mmol), TBN (16 mol%), HCl (5 mol%) and catalyst (1.5-2 mol%) in toluene (0.5 mL) in a flask was charged with pure oxygen (balloon filled, 621-622 torr O_2). The resulting mixture was stirred at 50 °C for the time indicated in Table 4. Progress of the reaction was monitored by GC. After completion of the reaction, the heterogeneous catalyst simply separated from the reaction media by filtration. Then, the resulting solution evaporated to remove the solvent under reduced pressure. The obtained residue was directly characterized by NMR analysis without any more purification (Fig. S3).

Proposed mechanism to the synthesis of self-esterification products of aerobic oxidation of primary aliphatic alcohol over ABNO@PMO-IL-Br catalyst

We postulate that the lower activity of an aliphatic alcohol, in comparison with activated benzyl alcohols, enables self-esterification likely via further oxidation of corresponding hemi-acetal (II) formed upon reaction of intermediate (I) in Scheme S1 with a second alcohol substrate under acidic reaction conditions.



Scheme S1: Schematic diagram of postulated mechanism of self-esterification of primary aliphatic alcohol over ABNO@PMO-IL-Br catalyst

Fig. S1 Thermal gravimetric analysis (TGA) of synthesized materials (PMO-IL and ABNO@PMO-IL-Cl).



TGA diagram of PMO-IL







TGA of synthesized materials PMO-IL and ABNO@PMO-IL.

 Table S1. Elementary analysis of the materials

Material	С%	Н%	N%
PMO-IL	11.77	0.98	2.37
ABNO@PMO-IL	15.51	0.98	3.10

Fig. S2 (a) FTIR spectra of synthesized 3-oxo-ABNO, PMO-IL and ABNO@PMO-IL; (b) FT-IR spectrums of synthesized material (ABNO@PMO-IL-Cl).



(a) FTIR spectra of synthesized 3-oxo-ABNO, PMO-IL and ABNO@PMO-IL



(b) FT-IR spectrum of ABNO@PMO-IL-Cl



Fig. S3 ¹H NMR and ¹³C NMR spectrums of ester products in CDCl₃.





DEPT Spectrum of Compound in CDCl₃













DEPT Spectrum of Compound in CDCl₃

f1 (ppm)

2.5

4.0

5.0

3.5

2.0

1.5

1.0

0.5

Fig. S4-S29 Gas chromatogram results of Table 3

Determination of the product yields by GC chromatograms:

initially, three blank solutions of an equal mixture of benzyl alcohol and benzaldehyde (1:1) with three different equimolar ratios (i.e 0.125 mmol, 0.250 mmol, and 0.500 mmol) were prepared in EtOAC (2 mL) and each solution were then analyzed by GC. The ratios of alcohol/aldehyde and the results of all GC chromatograms were collected in Fig. S4. As can be clearly seen, in all the GC chromatograms of blank solutions containing 0.5, 0.25 and 0.125 mmol benzyl alcohol and benzaldehyde, respectively, the sensitivity of FID detector of our GC instrument was adjusted (calibrated) to a level in which the response to benzaldehyde and benzyl alcohol is very close to 1 (1.01 as average of three experiments demonstrated in Figs. S4-1, S4-2, S4-3). In a separated experiment, a blank solution of an equimolar mixture of acetophenone and 1phenylethanol with a mole ratio of (0.125 mmol) was analyzed by GC under the same conditions (Fig. S4-4). Again, the results showed that the FID detector (at the adjusted sensitivity level) exhibited the same sensitivity to ketone (acetophenone) in comparison with its related alcohol (1-phenylethanol). After calibrating the FID detector and by considering the fact that, the GC instrument showed very close sensitivity toward alcohols and their corresponding carbonyl compounds within the experimental error of the employed GC instrument, for the subsequent studies the GC outcomes (chromatograms) were used to estimate the product yields.

Fig. S4-1 Gas chromatogram of the solution contains 0.5 mmol benzyl alcohol and benzaldehyde (1:1)

Fig. S4-2 Gas chromatogram of the solution contains 0.25 mmol benzyl alcohol and benzaldehyde (1:1)

Fig. S4-3 Gas chromatogram of the solution contains 0.125 mmol benzyl alcohol and benzaldehyde (1: 1)

The average integral of benzaldehyde/benzyl alcohol in all solutions: Obtained from S4-1, S4-2 and S4-3 = 1.01

Fig. S4-4 Gas chromatogram of the solution contains 0.125 mmol 1-phenyl-1-ethanol and benzophenone (1:1)

Fig. S5 Gas chromatogram for the oxidation of benzyl alcohol (Table 3 Entry 1)

Fig. S6 Gas chromatogram for the oxidation of 4-methylbenzyl alcohol (Table 3 Entry 2)

Fig. S7 Gas chromatogram for the oxidation of 3-methylbenzyl alcohol (Table 3 Entry 3)

Fig. S8 Gas chromatogram for the oxidation of 2-methylbenzyl alcohol (Table 3 Entry 4)

Fig. S9 Gas chromatogram for the oxidation of 4-isopropylbenzyl alcohol (Table 3 Entry 5)

Fig. S10 Gas chromatogram for the oxidation of 4-chlorobenzyl alcohol (Table 3 Entry 6)

Fig. S11 Gas chromatogram for the oxidation of 3-chlorobenzyl alcohol (Table 3 Entry 7)

Fig. S12 Gas chromatogram for the oxidation of 2-chlorobenzyl alcohol (Table 3 Entry 8)

Fig. S13 Gas chromatogram for the oxidation of 4-bromobenzyl alcohol (Table 3 Entry 9)

Fig. S14 Gas chromatogram for the oxidation of 2-bromobenzyl alcohol (Table 3 Entry 10)

Fig. S15 Gas chromatogram for the oxidation of 2, 4-dichlorobenzyl alcohol (Table 3 Entry 11)

Fig. S16 Gas chromatogram for the oxidation of 4-nitrobenzyl alcohol (Table 3 Entry 12)

Fig. S17 Gas chromatogram for the oxidation of 3-nitrobenzyl alcohol (Table 3 Entry 13)

Fig. S18 Gas chromatogram for the oxidation of 2-nitrobenzyl alcohol (Table 3 Entry 14)

Fig. S19 Gas chromatogram for the oxidation of 4-methoxybenzyl alcohol (Table 3 Entry 15)

Fig. S20 Gas chromatogram for the oxidation of 2-methoxybenzyl alcohol (Table 3 Entry 16)

Fig. S21 Gas chromatogram for the oxidation of 4-(methylthio)benzyl alcohol (Table 3 Entry 17)

Fig. S22 Gas chromatogram for the oxidation of 1-naphthyl methanol (Table 3 Entry 18)

Fig. S23 Gas chromatogram for the oxidation of 1-phenyl-1-ethanol (Table 3 Entry 19)

Fig. S24 Gas chromatogram for the oxidation of 1-([1,1'-biphenyl]-4-yl)ethanol (Table 3 Entry 20)

Fig. S25 Gas chromatogram for the oxidation of 1-phenyl-1-propanol (Table 3 Entry 21)

Fig. S26 Gas chromatogram for the oxidation of benzhydrol (Table 3 Entry 22)

Fig. S27 Gas chromatogram for the oxidation of cyclopentyl(phenyl)methanol (Table 3 Entry 23)

Fig. S28 Gas chromatogram for the oxidation of α-Tetralol (Table 3 Entry 24)

Fig. S29 Gas chromatogram for the oxidation of 2-heptanol (Table 3 Entry 25)

Fig. S30 Gas chromatogram for the oxidation of 2-octanol (Table 3 Entry 26)

			Ret.	Time	Width			
Peak	Peak	Result	Time	Offset	Area	Sep.	1/2	Status
No.	Name	()	(min)	(min)	(counts)	Code	(sec)	Codes
1		96.483	3.596	0.000	1747529	BB	7.5	
2		3.517	4.968	0.000	63696	BB	8.6	
	Totals:	100.000		0.000	1811225			

Fig. S31 Gas chromatogram for the oxidation of 1-cyclohexylethanol (Table 3 Entry 27)

Fig. S32 Gas chromatogram for the oxidation of cycloheptanol (Table 3 Entry 28)

Fig. S33 Gas chromatogram for the oxidation of 2-adamantanol (Table 3 Entry 31)