

Visible light-promoted enantioselective aerobic oxidation of pyrazolones by phase transfer catalysis

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ABSTRACT

An efficient and enantioselective aerobic oxidation of 4-substituted pyrazolones has been developed by phase transfer catalysis. Using visible light as the driving force and O₂ (in air) as the oxidant, broad scopes (38 examples) of pyrazolones bearing an oxygen-attached carbon stereocenter at C-4 position were obtained in high yields (up to 98%) and excellent enantioselectivities (up to 93% *ee*) under mild conditions. The ready availability of catalyst, ease of operation, and low-cost and eco-friendly nature highlighted the practical utility of this visible light-promoted enantioselective aerobic oxidation.

Over the past several decades, visible light-promoted reactions have received much attention in modern chemistry. Moreover, enormous research interest in visible light-promoted asymmetric synthesis has been shown in recent years [1–6]. Among the photo-chemical reactions, visible light promoted aerobic oxidations have been emerging as one of the fastest growing fields in organic chemistry because of their low cost, easy availability and environmental friendliness [7]. From a green and sustainable point of view, the direct use of O₂ as an oxidant is the most ideal methodology for the development of oxygen-containing compounds [8–11]. Aerobic oxidations promoted by visible light mainly takes place through two modes: (a) alkyl radicals produced in the photocatalytic cycle can react with oxygen or peroxygen to introduce oxygen atoms; (b) molecular oxygen can be transferred from its non-excited triplet state (³O₂) to its more reactive singlet state (¹O₂) by photosensitization [12–17]. Thus, the utilization of inexpensive molecular oxygen as an environmentally friendly oxidant to develop efficient and green protocols for visible light-promoted aerobic oxidations is of great interest and highly desirable for future organic transformations [18–21].

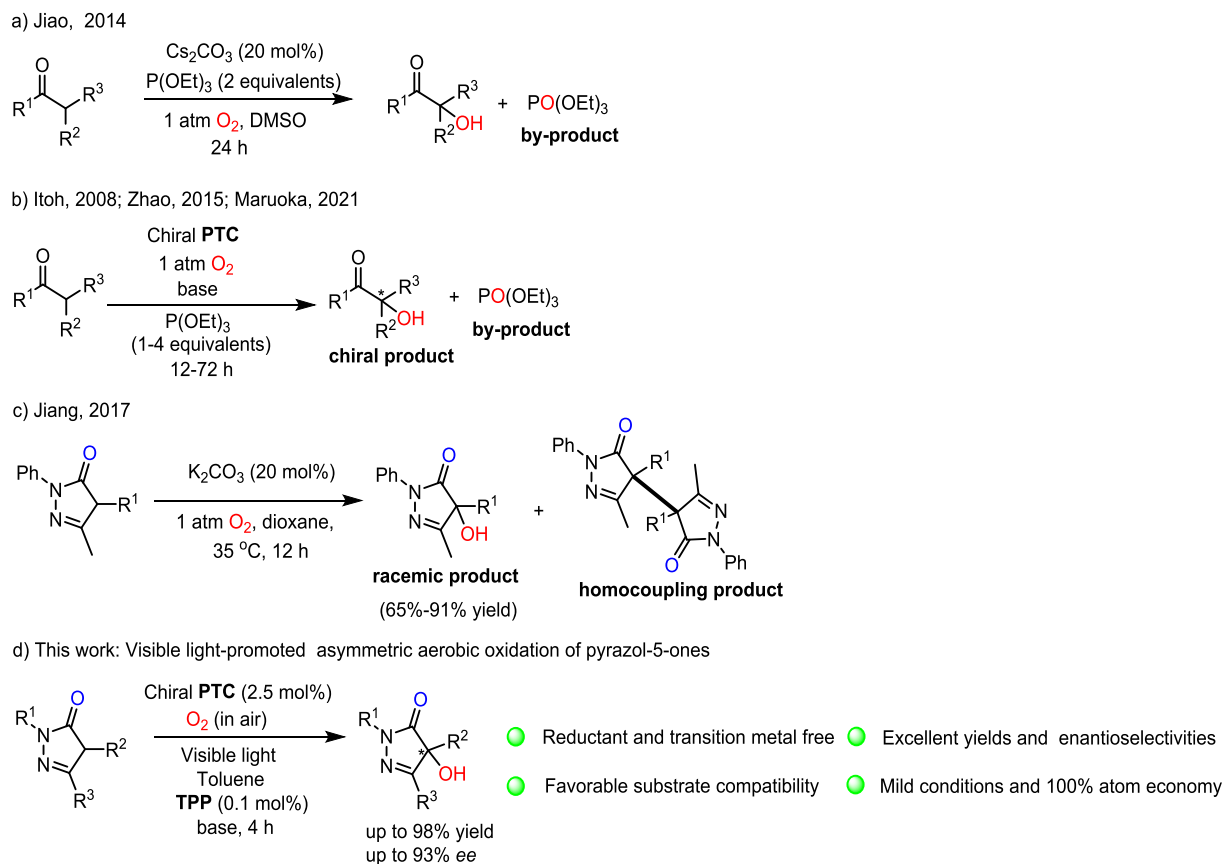
On the other hand, pyrazolone, especially for pyrazol-5-one skeleton, is a privileged five-membered nitrogen-containing pharmacophore in medicinal chemistry as its derivatives possessing many important biological properties [22], e.g., the first synthetic antipyretic and analgesic drug by Ludwig Knorr in 1883 [23,24], antibacterial agents [25], CCR₃ antagonist [26], antitumor agent [27], inhibitor of pancreatic lipase [28]

and carboxylesterase 2 [29]. Remarkable progress in asymmetric reactions of pyrazol-5-one and its common derivatives was achieved in recent years [30,31]. Concerning our sustaining interest in asymmetric aerobic oxidative reactions [32–34], we sought to develop a green and efficient method for asymmetric oxidation of pyrazoles. In recent years, the catalytic asymmetric α -hydroxylation of ketones, including oxindoles and β -keto esters with molecular oxygen have been particularly studied [35–46]. However, the aerobic oxygenation of α -C(sp³)-H bond in ketones was mostly initiated by bases, with excess phosphine reductants e.g. P(OEt)₃ added for high selectivity. Thus, it was appealing to develop a transition metal and reductant free asymmetric catalysis system to oxidize the tertiary C(sp³)-H bond in ketones [47–50], especially in pyrazol-5-ones. In 2016, Wang and co-workers reported an enantioselective hydroxylation at the C4-position of pyrazol-5-ones, with cumene hydroperoxide (CHP) as the oxidant [51]. Soon after, Jiang provided a practical aerobic oxidation of pyrazol-5-ones, but chiral products could not be obtained by this method, and homocoupling products were observed [52]. To the best of our knowledge, the asymmetric aerobic oxidation of pyrazol-5-ones (especially in air) is unprecedented and still remains a great challenge. Herein, we present the first visible light-promoted aerobic oxidation of pyrazol-5-ones to afford chiral 4-hydroxy-pyrazoles by phase transfer catalysis (Scheme 1).

Initially, pyrazol-5-one **1a** was chosen as the model substrate to optimize reaction conditions of visible light-promoted aerobic oxidation

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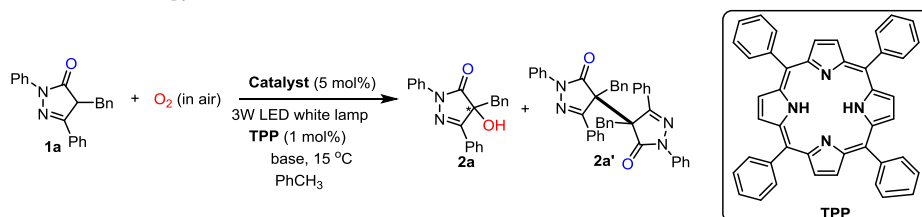
Scheme 1. Current approaches for catalytic aerobic oxidation of α -substituted α -hydroxy-ketones and 4-hydroxy-pyrazoles.

at 15 °C in toluene, treated with catalyst (5 mol%), tetraphenylporphine (TPP, 1 mol%), and base in air under 3 W LED (light-emitting diode) white lamp. The aerobic oxidation could not proceed without base and catalyst, but the unexpected homocoupling compound **2a'** was observed as the main product in 43% yield (Table 1, entry 1). When 30% K_2CO_3 was added, the oxidation product **2a** was obtained in 31% yield (Table 1, entry 2). We attempted to use the natural cinchona alkaloid quinidine (Cat 1) to control the enantioselectivity, but the results were not satisfactory (Table 1, entry 3). When the simple phase transfer catalysts (PTC) tetrabutylammonium bromide (TBAB), benzyltrimethylammonium bromide (BTMAB) were used, the α -hydroxylation product **2a** could be obtained in moderate yields, and homocoupling product **2a'** was not observed (Table 1, entries 4 and 5). Asymmetric phase transfer catalysis is recognized as an effective and sustainable method [53–55], and then we sought to use phase transfer catalysis to construct chiral oxygen-attached carbon stereocenter. First, we attempted to use the simple cinchona derivative **3a** as phase transfer catalyst to control the enantioselectivity (Fig. 1). Although the enantioselectivity was poor (11% *ee*), the reaction rate is obviously accelerated and **2a** was obtained in good yield (86%) (Table 1, entry 6). A series of cinchona alkaloid phase transfer catalysts were then screened. Among these, the doubly quaternized PTC (phase transfer catalyst) **3b** did not show good results (Table 1, entry 7) [56]. **3c** and **3d** with 3,5-(CF_3)₂ or 3,5-(OMe)₂ groups showed slightly higher *ee* values compared with that of **3a** (Table 1, entries 8 and 9). Interestingly, **3e** and **3f** with 3,5-(*t*Bu)₂ or 3,5-(phenyl)₂ groups, worked well and gave good enantioselectivities of 28%–32% *ee* (Table 1, entries 10 and 11). We also tested the hybrid amide-based PTC **3g** [57] and the dimeric PTC **3h** [58], but they did not reveal good results

(Table 1, entries 12 and 13). Notably, an obvious improvement of enantioselectivity had been achieved by introducing a 9-anthracenyl-methyl group. The quinidine and cinchonine derived PTC **3i** and **3k** [59], the *N*-oxide PTC **3j** [60], and the C-2'-arylated PTC **3l** [33] were tested, and we were surprised to find that the reactions proceeded faster (84%–95% yield, 2 h) and with higher enantioselectivity (39%–57% *ee*) (Table 1, entries 14–17). To our disappointment, PTC **3m**, which has hydroxy groups at both the C-9 and the C-6' positions, showed poor results (Table 1, entry 18). PTC **3n**, which has a bulky 1-adamantyl group at the C-9 position [61], was then screened, but the *ee* value was notably lower than that obtained with **3k** (Table 1, entry 19), which supported that the free hydroxy group at the C-9 position was responsible for inducing high enantioselectivity in the reaction process. Finally, the cinchonidine and quinine derived PTC **3o** and **3p** afforded high reactivity and selectivity (91%–93% yield, 47%–51% *ee*) and provided the reversed *R*-product of **2a**.

After PTC **3k** had been identified as a suitable catalyst, further reaction optimizations were undertaken. We summarize the effects of several parameters on this reaction (Table 2). First, several bases were screened in toluene in the presence of **3k**. The use of 50% K_2HPO_4 led to a longer reaction time compared with 30% K_2CO_3 (Table 2, entries 1 and 2). When the stronger bases (30% Cs_2CO_3 , 10% $CsOH$ and 10% KOH) were used, the reactions proceeded faster (89%–96% yield, 30 min) and the *ee* values of **2a** were noticeably improved (66%–74% *ee*) (Table 2, entries 4–6). Solid KOH provided **2a** in high yield with relatively moderate enantioselectivity (Table 2, entry 7). It is worth mentioning that the *ee* value was improved to 86% when the reaction temperature was decreased to –20 °C (Table 2, entry 8). Further study showed that the

Table 1
Screening of catalysts for aerobic oxidation of pyrazolone **1a**^a.



Entry	Catalyst	Base	Time (h)	Yield (%) 2a/2a' ^b	ee (%) ^c
1	-	-	24	43/Trace	Nd
2	-	30% K_2CO_3	24	31/13	Nd
3	Cat 1	-	24	36/24	3 (S)
4	TBAB	30% K_2CO_3	6	51/Trace	0
5	BTMAB	30% K_2CO_3	6	62/Trace	0
6	3a	30% K_2CO_3	2	86/Trace	11 (S)
7	3b	30% K_2CO_3	4	67/Trace	14 (S)
8	3c	30% K_2CO_3	2	88/Trace	23 (S)
9	3d	30% K_2CO_3	12	64/Trace	13 (S)
10	3e	30% K_2CO_3	2	91/Trace	28 (S)
11	3f	30% K_2CO_3	2	93/Trace	32 (S)
12	3g	30% K_2CO_3	12	53/Trace	7 (S)
13	3h	30% K_2CO_3	2	92/Trace	11 (S)
14	3i	30% K_2CO_3	2	91/Trace	46 (S)
15	3j	30% K_2CO_3	2	84/Trace	39 (S)
16	3k	30% K_2CO_3	2	95/Trace	57 (S)
17	3l	30% K_2CO_3	2	93/Trace	49 (S)
18	3m	30% K_2CO_3	12	42/Trace	11 (S)
19	3n	30% K_2CO_3	6	67/Trace	8 (S)
20	3o	30% K_2CO_3	2	93/Trace	51 (R)
21	3p	30% K_2CO_3	2	91/Trace	47 (R)

^a Unless otherwise specified, pyrazol-5-one **1a** (0.1 mmol), catalyst (0.005 mmol, 5 mol%), and TPP (0.001 mmol) were added to a test tube equipped with a stirring bar and dissolved in toluene (10 mL). Then, 30% K_2CO_3 (0.5 mL) was added. The mixture was stirred in air with exposure to a 3 W LED white lamp at 15 °C in air until the reaction was completed.

^b Isolated yields.

^c Determined by HPLC analysis (Chiralcel OJ-H) with hexane/2-propanol (90 : 10) as the eluent.

sensitizer TPP (tetraphenylporphine) loading could be decreased to as low as 0.1 mol%, catalyst loading could be decreased to 2.5 mol%, while maintaining a comparable reaction conversion and achieving a high *ee* value to 89% in 4 h (Table 2, entry 9). The use of pure oxygen would obviously lead to a faster reaction rate. Under the standard conditions, **1a** was nicely converted into **2a** in 60 min, but the *ee* value was decreased to 84% accordingly (Table 2, entry 9). Considering the economy, practicability and enantioselectivity, we still choose air as the most suitable oxidant. Furthermore, the enantioselectivity could be improved to 89% when the reaction temperature was decreased to -40 °C using *m*-xylene as the solvent, but the reaction time was extended to 12 h, and we can clearly observe the existence of active intermediate peroxide by HPLC. This interesting phenomenon would be discussed later (Table 2, entry 12). To our delight, the reaction proceeded well in the sunlight and gave the corresponding product **2a** in almost quantitative yield with 84% *ee* after 6 h (Table 2, entry 14). Other sensitizers were also tested. It was found that Rose Bengal [62] and phthalocyanine [63] showed a considerable reactivity, whereas $[Ru(bpy)_3]Cl_2$ [64] and I_2 [65,66] showed poor results (Table 2, entries 15–18). The reason for the significant differences in reactivity among these sensitizers may have been due to the two different reaction mechanisms. Hence, the reaction parameters listed in entry 9 were selected as the optimal reaction conditions for the next investigations.

With the optimal conditions in hand, the substrate generality of pyrazolone was further explored. The results are summarized in Scheme 2. Initially, with the benzyl group at the 4-position, the substituent effect of the aryl ring was investigated. Both the electron donating and electron withdrawing groups were tolerated, such as 3-OMe, 3-CF₃, 4-Me, 4-NO₂ and 4-CF₃, affording the corresponding products in the excellent yields

(86%–98%) and good enantioselectivities (63%–89% *ee*) (Scheme 2, **2a–2f**). Then we observed 3,5-di-CF₃, 3,5-di-OMe, 3,5-di-F, 3,5-di-Br and 3,5-di-*t*-Bu are all well-tolerated and the oxidation products were obtained in good yields with 81%–88% *ee* (Scheme 2, **2g–2j**). However, when **1k** with 2-OMe and 5-F in the benzyl position was tested, the *ee* value was decreased significantly. The naphthalene contained substrate **1l** afforded **2l** with 81% *ee*. It is worth mentioning that **2m** could be easily obtained in 78% yield with 99% *ee* by simple recrystallization. To our disappointment, methyl and propargyl substitution at the 4-position of pyrazolone framework exhibited low levels of enantioselectivity (Scheme 2, **2n–2o**). These results indicated that a π - π stacking interaction between the PTC and the benzyl position might exist. In Jiang and Wang's work, most of the pyrazoles were screened at C-4-position, but the C-3-position was less explored [51,52]. In order to further expand the scope of this reaction and enhance the structural diversity of the products, the substituted groups at the 3-position were then investigated. First, the methyl group at 3-position afforded poor enantioselectivity (34% *ee*), although the hydroxylated product **2p** was obtained in 97% yield. Then the substituent effect of the aryl ring at C-3 position was investigated. Remarkably, 4-F, 4-Cl, 4-Me, 4-Ph, naphthyl, 4-isopropyl, 4-CN, 3,5-di-OMe, 3,5-di-CF₃, 3-F, 3-Br, 3-CF₃, 2-OMe in aryl ring at C-3 position are all well-tolerated and the hydroxylated product were obtained in 89%–98% yield with 79%–93% *ee* (Scheme 2, **2q–2ad**). Also, the chlorine and bromine substitution on the aryl group provided facile synthetic handles for further derivatization. Next we investigate the influence of the *N*-substituents (*R*₁), which is not fully explored yet. To our delight, varying the *N*-substituents (*R*₁) of **1** also afforded a high level of efficiency (92%–97% yield) and enantioselectivity (80%–90% *ee*) (Scheme 2, **2ae–2ak**). However, when the 2-F benzyl was introduced, the enantioselectivity of **2al** was significantly decreased.

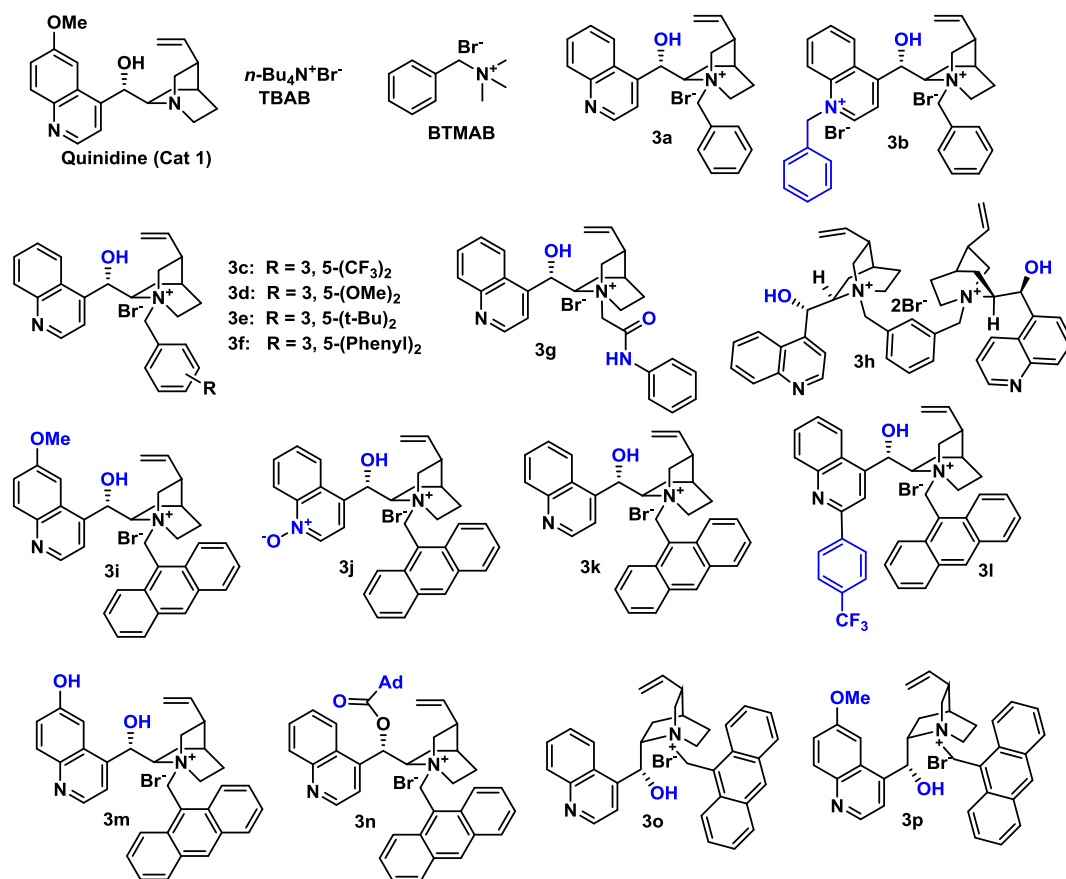
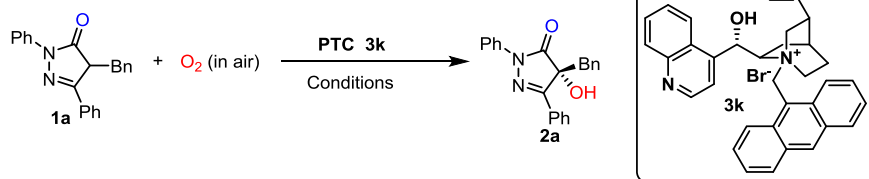


Fig. 1. Catalysts employed for the visible light-promoted asymmetric aerobic oxidation of pyrazolone **1a**.

Table 2

Optimization of the reaction conditions for the aerobic oxidation of pyrazolone **1a**.^a



Entry	Light source	Solvent	PTC 3k (mol%)	Base	Photosensitizer	Temp (°C)	Reaction time	Yield ^{ab} (%)	ee ^c (%)
1	3-W LED white lamp	PhMe	5	30% K ₂ CO ₃	TPP (1 mol%)	15	60 min	95	58
2	3-W LED white lamp	PhMe	5	50% K ₂ HPO ₄	TPP (1 mol%)	15	12 h	75	43
3	3-W LED white lamp	PhMe	5	30% K ₂ CO ₃	TPP (1 mol%)	0	2 h	85	62
4	3-W LED white lamp	PhMe	5	10% Cs ₂ CO ₃	TPP (1 mol%)	0	60 min	89	66
5	3-W LED white lamp	PhMe	5	10% CsOH	TPP (1 mol%)	0	60 min	95	71
6	3-W LED white lamp	PhMe	5	10% KOH	TPP (1 mol%)	0	30 min	96	74
7	3-W LED white lamp	PhMe	5	Solid KOH ^d	TPP (1 mol%)	0	30 min	96	52
8	3-W LED white lamp	PhMe	5	10% KOH	TPP (1 mol%)	-20	30 min	95	86
9	3-W LED white lamp	PhMe	2.5	10% KOH	TPP (0.1 mol%)	-20	4 h (60 min) ^e	95 (88) ^c	89 (84) ^c
10	3-W LED white lamp	PhMe	0.5	10% KOH	TPP (0.1 mol%)	-20	24 h	68	81
11	3-W LED white lamp	PhMe	2.5	40% KOH	TPP (0.5 mol%)	-40	12 h	81	86
12	3-W LED white lamp	<i>m</i> -Xylene	2.5	40% KOH	TPP (0.5 mol%)	-40	12 h	84	89
13	100 W halogen lamp	PhMe	2.5	10% KOH	TPP (0.1 mol%)	-20	4 h	92	82
14	Sunlight	PhMe	2.5	10% KOH	TPP (0.1 mol%)	-20	6 h	88	84
15	3-W LED white lamp	PhMe	5	10% KOH	Rosebengal (1 mol%)	-20	6 h	83	71
16	3-W LED white lamp	PhMe	5	10% KOH	Phthalocyanine (1 mol%)	-20	6 h	78	76
17	3-W LED white lamp	PhMe	2.5	10% KOH	[Ru(bpy) ₃]Cl ₂ (1 mol%)	-20	8 h	Trace	Nd
18	3-W LED white lamp	PhMe	2.5	10% KOH	I ₂ (1 mol%)	-20	4 h	Trace	Nd

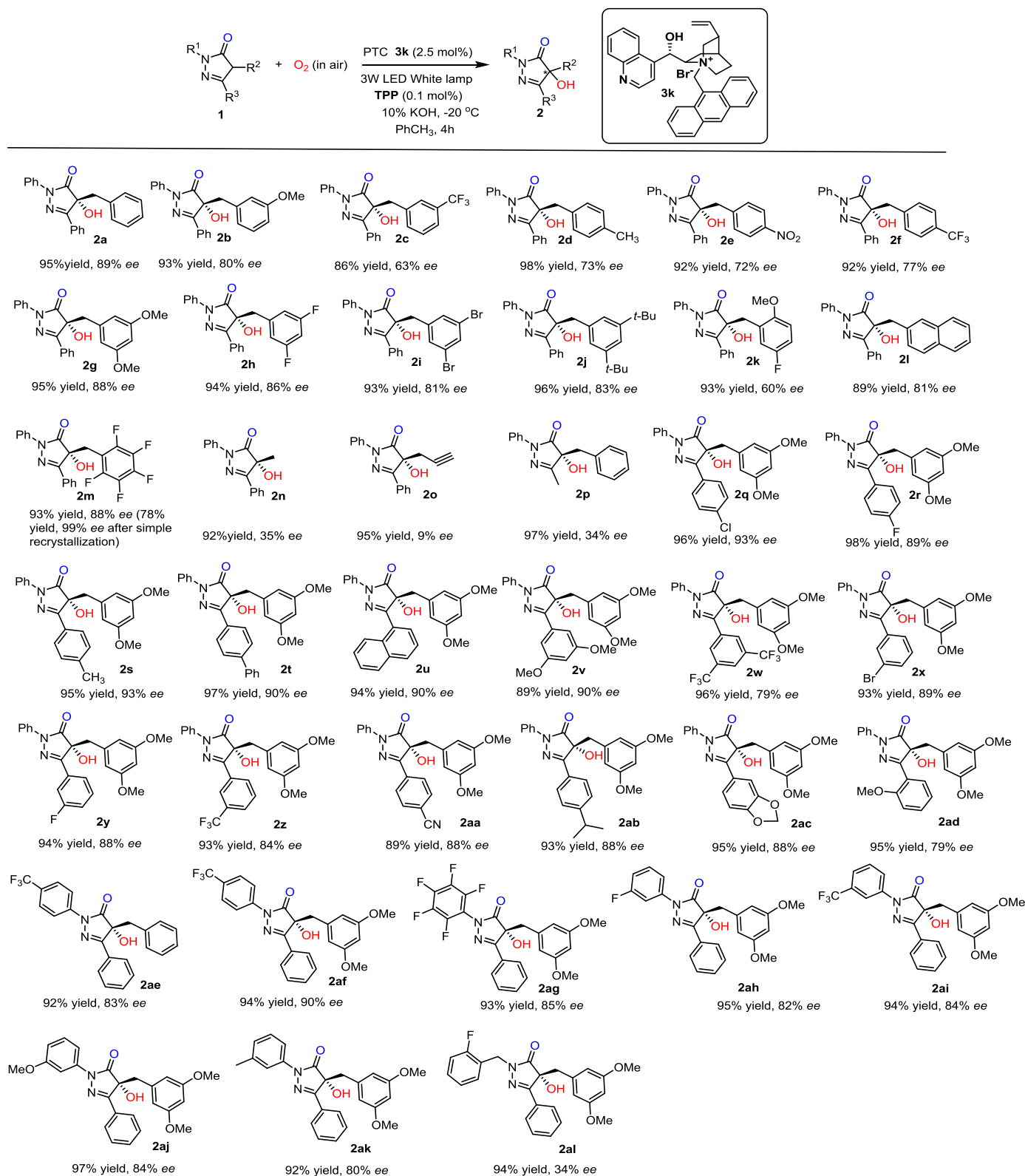
^a Unless otherwise specified, the reaction was performed with 0.1 mmol of **1a** by using the same conditions described in Table 1.

^b Yields shown are of isolated products.

^c Determined by HPLC analysis (Chiralcel OJ-H) with hexane/2-propanol (90:10) as the eluent.

^d 3 equiv. of the base was used.

^e Using pure oxygen gas as the oxidant.



Scheme 2. Generality of the asymmetric hydroxylation of pyrazolone. The reaction was conducted with pyrazolones **1** (0.1 mmol) in the presence of PTC **3k** (2.5 mol%) and TPP (0.01 mol%) in a PhCH₃ (10 mL) and KOH (0.5 mL, 10% aq.) at -20 °C, with exposure to a 3 W LED white lamp under air for the 4 h. Yield of isolated product. Enantiomeric ratios were determined by HPLC analysis of the product using a chiral column (DAICEL Chiralcel OD-H, AD-H, or AS-H) with *n*-hexane/2-propanol as the eluent.

Above all, this method showed good substrate suitability of various pyrazolones using an operationally simple and economical method.

In order to gain deep insights into the photo-oxidation mechanism of pyrazolones, a set of trapping and control experiments were carried out using **1a** as the model substrate. Nearly no reaction took place in the dark. When the reaction was shielded by Ar, the visible light-promoted aerobic oxidation could not proceed. These results indicated that O₂ (in air) and light are essential for this reaction (Table 3, entries 1 and 2). The photo-oxidation of **1a** proceeded with equal efficiency using TEMPO or BHT as an additive. These two experimental observations argue against a radical-based mechanism (Table 3, entries 3 and 4). However, when 1,4-diazabicyclo[2.2.2]-octane (DABCO) was added, the yield of product decreased dramatically, affording product **2a** in only 17% yield, suggesting that a singlet oxygen process might be involved in the present reaction (Table 3, entry 5). Furthermore, the reaction did not take place in the absence of TPP, and the homocoupling compound **2a'** was observed as the main product (Table 3, entry 6). We also tried the successful reported reaction conditions (P(OEt)₃/O₂) for the aerobic oxidation. Although the P(OEt)₃/O₂ system was successfully applied in the enantioselective α -hydroxylation of oxindoles [36], aromatic acyclic and cyclic ketones [38] and aryl- δ -lactams [39], this system was not efficient for the aerobic oxidation of pyrazolone (Table 3, entry 7). Then we use cumene hydroperoxide (CHP) as the oxidant, we were surprised to see that the α -hydroxylation product was obtained in 71% yield with 37% *ee* when CHP was used as the oxidant (Table 3, entry 8). These results indicated the active peroxide intermediate **4a** might be the key intermediate for this aerobic oxidation.

In order to verify the existence of active peroxide intermediate **4a**, we did some control experiments as shown in Table 4. The substrate concentration was reduced from 0.01 mol/L to 0.004 mol/L. We did the aerobic photo-oxidations at different temperatures. We can clearly observe the existence of active intermediate **4a** by HPLC and HRMS when the temperature drops to -40 °C after 4 h (**2a/4a** = 91/9). When the temperature was decreased to -78 °C, the formation rate of peroxide intermediate **4a** could be significantly increased (**2a/4a** = 42/58) (Table 4, entries 1–5). Next, we want to verify whether the peroxide **4a** could oxidize **1a** or not. After the reaction was completed in -60 °C (Table 4, entry 4), 0.05 mmol of **1a** was added in the reaction system without light under Ar atmosphere, and the peroxide **4a** was significantly

Table 3
Asymmetric aerobic oxidation of pyrazolone **1a** under some special conditions^a.

Entry	Addition of condition	Yield ^b (%)	<i>ee</i> ^c (%)
1	In the dark instead of light	Trace	Nd
2	Ar instead of air	Nr	Nd
3	TEMPO (2.0 equiv.)	81	86
4	BHT (2.0 equiv.)	83	84
5	DABCO (2.0 equiv.)	17	Nd
6	Without TPP	Trace	Nd
7 ^d	P(OEt) ₃ (2.0 equiv.) instead of TPP, O ₂ (1 atm)	36	12
8 ^d	CHP (2.0 equiv.) instead of TPP, Ar instead of air and light	71	37

^a Unless otherwise specified, the reaction was performed with 0.1 mmol of **1a** by using the same conditions described in Scheme 2.

^b Yields shown are of isolated products.

^c Determined by HPLC analysis.

^d Reaction time: 12 h.

decreased in 1 h. After 4 h, nearly no peroxide **4a** could be seen in the reaction system (Table 4, entries 6 and 7). These findings indicated the peroxide **4a** would react with **1a**, which give the final product **2a** (see Supporting information for details).

To test the scale-up potential of our methodology, a 2.32 g sample (5 mmol%) of pyrazolone **1x** was treated with PTC **3k** (2.5 mol%) and TPP (0.1 mol%) on a gram-quantity scale in toluene (200 mL) and an aqueous solution containing 10% KOH (20 mL) under mild conditions. The reaction was exposed to a 25 W LED white lamp in air at -20 °C. After 12 h, the reaction was completed and the α -hydroxylation product was obtained by chromatography in 87% yield with 85% *ee* (Scheme 3). The chiral hydroxy group of **2x** could be easily transformed to azido, triazole and *O*-mesyl groups. Furthermore, the absolute configuration of **2a** was determined to be *S* by comparing the HPLC spectra and optical rotation with the reported example [51]. The absolute configurations of other products were assigned accordingly.

On the basis of these experiments and the related reported work, we proposed a possible mechanism for this asymmetric photo-oxidation of pyrazolone. The molecular oxygen in air could be easily transferred from its non-excited triplet state (³O₂) to its more reactive singlet state (¹O₂) by photosensitization with light [12]. Then, deprotonation of **1** quickly occurred in the presence of base. The chiral enolate-PTC complex could have formed and reacted with the active singlet molecular oxygen (¹O₂), thereby resulting in the formation of the active peroxide intermediate **4** [33,52]. The active peroxide intermediate **4** could be rapidly converted into the final chiral α -hydroxylation product **2** in the second step (Scheme 4).

In conclusion, we have disclosed a highly efficient and practical asymmetric visible light-promoted aerobic oxidation of pyrazolones by phase transfer catalysis. A wide range of chiral α -hydroxy 4-substituted pyrazolones (38 examples) can be obtained with excellent yields and enantioselectivities under reduct and transition metal free conditions with relatively low catalyst and photosensitizer loadings. Furthermore, this asymmetric aerobic oxidation is inexpensive, operationally simple, and environmentally benign. Further research on expanding the applications of asymmetric visible light-promoted aerobic oxidation by phase transfer catalysis are currently underway in our laboratory.

Table 4
Control experiments for aerobic oxidation of pyrazolone^a.

Entry	Temp (°C)	2a/4a ^b	<i>ee</i> ^b (%)
1	-20	100/0	82
2	-40	91/9	81
3	-50	89/11	77
4 ^c	-60	66/34	79
5 ^c	-78	42/58	79
6 ^{c,d}	-60	92/8 ^e	77 ^e
7 ^{c,d}	-60	100/0 ^f	72 ^f

^a Unless otherwise specified, pyrazol-5-one **1a** (0.1 mmol), catalyst (0.005 mmol, 5 mol%), and TPP (0.001 mmol) were added to a test tube equipped with a stirring bar and dissolved in toluene (25 mL). Then, 40% KOH (1 mL) was added. The mixture was stirred in air with exposure to a 7 W Led white lamp in air for 4 h.

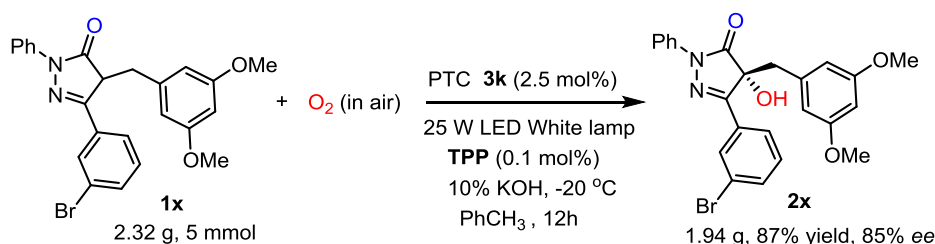
^b Determined by HPLC analysis.

^c 3 Equivalent of solid KOH was used instead of 40% KOH.

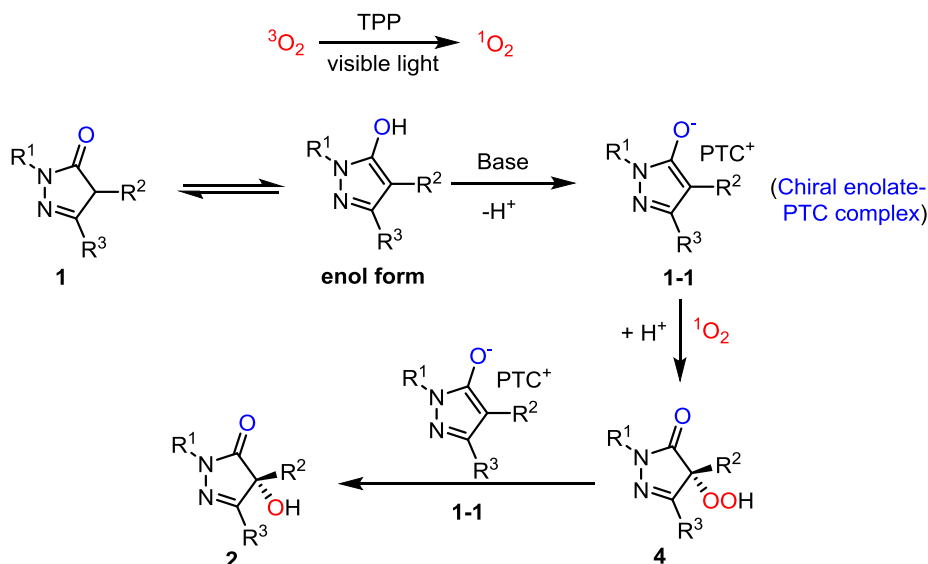
^d After the reaction was completed, 0.05 mmol of **1a** was added in the reaction system without light under Ar atmosphere.

^e After the addition of **1a** for 1 h.

^f After the addition of **1a** for 4 h (Table S6 in Supporting information for details).



Scheme 3. Scaled-up version of the reaction.



Scheme 4. Proposed mechanism for visible light-promoted aerobic oxidation of pyrazolone.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gresc.2021.11.004>.

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