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Tetra-*n*-butylammonium Bromide: A Simple but Efficient Organocatalyst for Alcohol Oxidation under Mild Conditions

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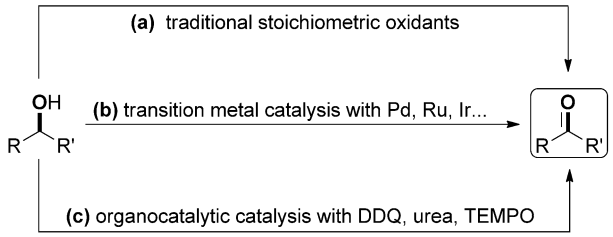
Abstract: A simple but efficient organocatalytic system with 5 mol% tetra-*n*-butylammonium bromide (TBAB) as the catalyst has been identified for alcohol oxidation for the first time. This organocatalytic system is compatible with a broad range of benzylic/allylic alcohols with various catalytically reactive groups. Besides, it shows excellent selectivity for secondary benzylic alcohols over aliphatic alcohols, and good selectivity over the primary benzylic alcohol site in 4-(1-hydroxyethyl)benzyl alcohol. Thus, the features of simplicity, high efficiency, selectivity and mildness of reaction conditions associated with this TBAB organocatalytic system suggest its potential for widespread use in synthetic chemistry.

Keywords: acetophenone; α-hydroxybenzyl cation; α-hydroxybenzyl radical; organocatalysts; selective alcohol oxidation

The oxidation of alcohols to aldehydes and ketones is among the most important and widely used synthetic operations in both laboratory and industrial fields, and has been attracting considerable attentions from synthetic chemists.[1] Thus, a variety of classical strategies were developed for this transformation with the use of traditional stoichiometric oxidants such as active manganese dioxide,[2] chromium-based oxidants,[3] "activated dimethyl sulfoxide",[4] and hypervalent iodine reagents (Scheme 1a).[5] During the last decades, many efficient transition metal catalysis systems have been developed for alcohol oxidation, including palladium,[1c–h,6] ruthenium,[1,7] iridium,[1,7] silver,[8] iron,[9] and vanadium complexes,[10] as well as some nanoparticles of these catalysts (Scheme 1b).[11] Of particular interest are catalysis systems employing cheap metal salts, together with nitroxyl radicals.[12] For example, in 2011 and 2013, the Stahl group

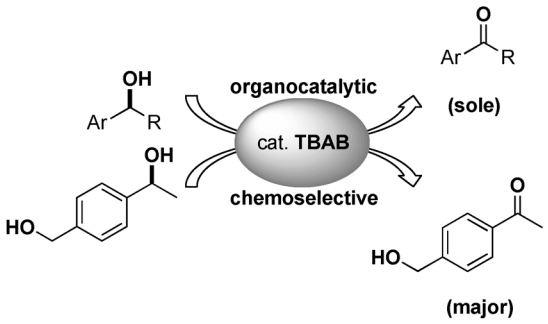


Scheme 1. Previous work on alcohol oxidation.

discovered that (bpy)Cu(OTf)/TEMPO/NMI[13] (where TEMPO = 2,2,6,6-tetramethylpiperidyl-1-oxyl, NMI = *N*-methylimidazole) and (^{MeO}bpy)Cu(OTf)/ABNO[14] (^{MeO}bpy = 4,4′-dimethoxy-2,2′-bipyridine; ABNO = 9-azabicyclo[3.3.1] nonane *N*-oxyl) catalytic systems could promote the efficient oxidation of a broad range of primary and secondary alcohols to the corresponding aldehydes and ketones at room temperature under aerobic conditions.

To obtain more practical and efficient processes, especially with high chemoselectivity, and to accommodate more challenging substrates for alcohol oxidations, chemists have paid much attention to non-metal catalytic systems for the advantages inherent in them (Scheme 1c). Researchers found that using DDQ,[15] thiourea,[16] or quinine-derived ureas[17] as organocatalyst revealed certain reactivities, while using nitroxyl radicals afforded higher efficiency towards alcohol oxidations. For instance, the Hu[18] and Jahn[19] groups reported that TEMPO/*t*-BuONO or TEMPO/Br_2/$NaNO_2$ can promote the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. Also in 2013, by using a unique *N*-oxyl radical, namely 4-acetamido-TEMPO, the Stahl group identified an organocatalytic method for the chemoselective aerobic oxidation of secondary benzylic alcohols within lignin model compounds.[20]

However, to the best of our knowledge, few organocatalysts can enable the oxidation of alcohols, espe-



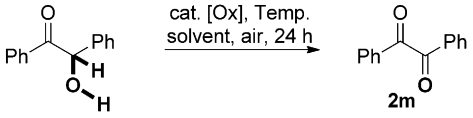
Scheme 2. TBAB-catalyzed alcohol oxidation (this work).

cially with remarkable chemoselectivities, among which only the modified TEMPO could meet this requirement. Hence, the search for a simple and efficient organocatalyst or organocatalytic process for selective alcohol oxidation is a highly desirable but challenging task. Very recently, our group disclosed that the TBAB/TBHP catalytic system can promote the formation of *t*-BuO$^{\bullet}$ radicals;[21] meanwhile, α-hydroxyalkyl radicals could be generated *via* reaction of the corresponding alcohols with alkoxyl radicals such as *t*-BuO$^{\bullet}$,[22] and might be oxidized to α-hydroxyalkyl cations in the presence of oxidants *via* a single-electron transfer (SET) process.[23] As such, it could be speculated that TBAB/TBHP might work as an efficient catalytic system for alcoholic hydroxy group transformations as well. *Herein, we have successfully apply TBAB as the simple but efficient organocatalyst for the oxidation of alcohols under mild conditions.* This strategy accommodates a variety of functionalized benzylic/allylic alcohols. Most importantly, it shows excellent selectivity for secondary benzylic alcohols over aliphatic alcohols, and good selectivity over the primary benzylic alcohol site in 4-(1-hydroxyethyl)benzyl alcohol (Scheme 2).

Our studies commenced by testing different ammonium halides (10 mol%) for the metal-free oxidation of benzoin (1 equiv.) in EtOAc (2.0 mL) at 30 °C with TBHP (5.0–6.0 M in decane, 2 equiv.) as the oxidant. As shown in Table 1, when this oxidation was carried out under an air or N_2 atmosphere without any ammonium halides, less than 5% of the desired benzil (**2m**) was detected (Table 1, entries 1 and 2). In contrast, the reaction efficiency increased dramatically when employing 10 mol% of an ammonium halide, such as TEAB, TBAI, or TBAB, as the organocatalyst and particularly TBAB gave the highest (69%) yield of the desired product **2m** (entries 3–5). Further optimizations are the focus of the ongoing investigations, and several preliminary observations can be made within the optimization process. When the reaction was conducted at 40 °C, the yield of **2m** was improved to 78% (entries 5–7). TBHP (70% aqueous solution) or TBP as oxidant was also evaluated at 40 °C, but the best result was still obtained with TBHP (5.0–6.0 M in decane) in combination with the organocatalyst TBAB (entries 6, 8 and 9). The oxidation efficiency shows a strong dependence on solvent. For example, a sharp decrease of the yield was observed when using acetonitrile, DCE, DCM or toluene as the solvent (entries 10–12, 15). Moreover, the oxidation nearly did not occur if conducting the reaction in THF or *p*-dioxane (entries 13 and 14). Fortunately, benzene as the solvent enhanced the oxidation efficiency greatly, giving **2m** in the highest yield of 90% among all the solvents examined (entry 16). Other endeavours to improve the yield of **2m** were attempted as well. For instance, lowering the catalyst loading to 5 mol% resulted in a slight increase of the catalytic reactivity, while a loading of 2.5 mol% or 20 mol% TBAB reduced the yield by about 30%, respectively (entries 16–19). Besides, nearly identical results were obtained when changing the amount of TBHP (5.0–6.0 M in decane). Thus, 1.0 equiv. and 3.0 equiv. of TBHP (5.0–6.0 M in decane) as oxidant reduced the oxidation efficiency to 65% and 80%, respectively (entries 17, 20 and 21). Shortening the reaction time lowered the oxidation outcome accordingly, whereas prolonging the reaction time had almost no effect on the reaction efficiency (entries 22 and 23).

With the optimized reaction conditions in hand, the substrate scope was explored at 40 °C for 24 h under air atmosphere, using 5 mol% TBAB as the organocatalyst, TBHP (5.0–6.0 M in decane, 2.0 equiv.) as the oxidant, and benzene (2.0 mL) as the solvent. As summarized in Scheme 3, this organocatalytic alcohol oxidation was successfully performed with secondary benzylic/allylic alcohols, affording the desired acetophenones in moderate to excellent yields. A range of functionalized alcohols underwent facile oxidations to the corresponding ketones in the presence of electron-withdrawing groups such as aryl chloride and aryl bromide (*cf.* **2b–d**), as well as electron-donating groups such as methyl, isopropyl, and methoxy groups (*cf.* **2e–g**), all of which have potential for additional functionalization of the products. Significant differences could be observed between substrates with different electronic and steric properties. Notably, those possessing an aromatic ring with electron-withdrawing groups displayed higher reactivities than those with electron-donating groups (*cf.* **2a–g**), and the reaction of 1-*ortho*-tolylethanol proceeded with a much slower reaction rate than did that of 1-*para*-tolylethanol because of steric hindrance (*cf.* **2e** and **2h**). The organocatalytic system also facilitates substrates bearing oxidatively sensitive functional groups, such as naphthyl (**2k**) and thienyl (**2l**). Specifically, the tolerance of internal alkenes afforded excellent yields of chalcone derivatives with promising antibacterial activities,[24] and the complete retention of (*E*)-alkene configuration demonstrates the mildness of the reaction condi-

Table 1. Reaction conditions optimization.[a]



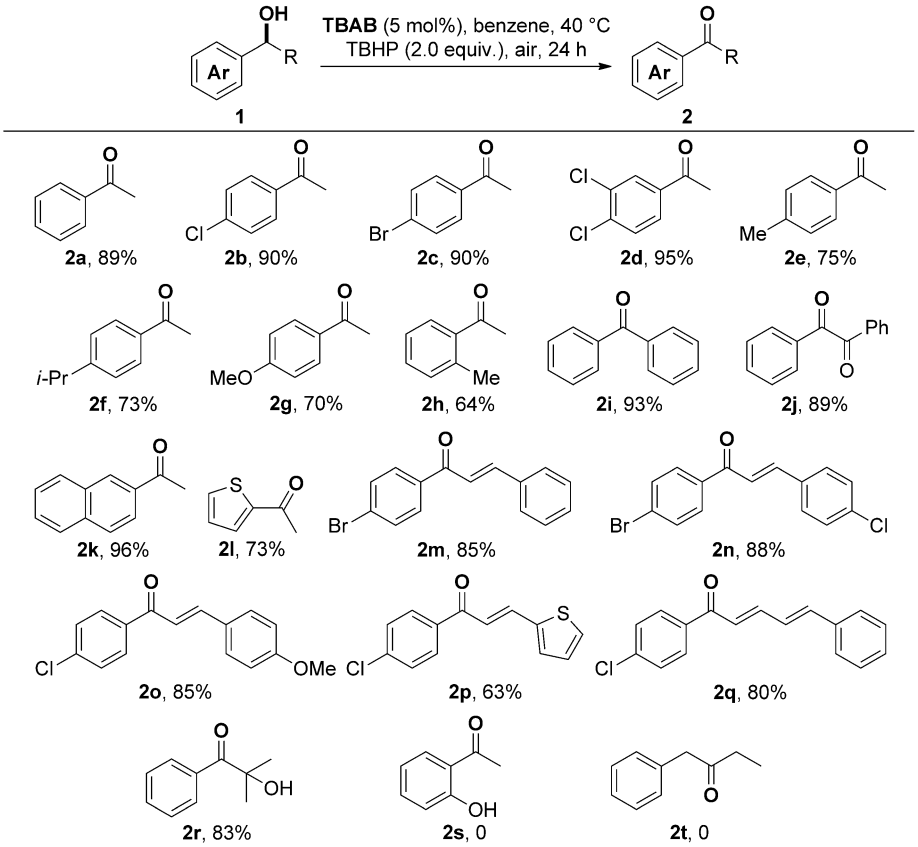
Entry	Cat. (mol%)	[Ox] (equiv.)	Solvent	Temp. [°C]	Yield [%][b]
1	–	$TBHP^{dec}$ (2.0)	EtOAc	30	<5
2[c]	–	$TBHP^{dec}$ (2.0)	EtOAc	30	<5
3	TEAB (10.0)	$TBHP^{dec}$ (2.0)	EtOAc	30	66
4	TBAI (10.0)	$TBHP^{dec}$ (2.0)	EtOAc	30	37
5	TBAB (10.0)	$TBHP^{dec}$ (2.0)	EtOAc	30	69
6	TBAB (10.0)	$TBHP^{dec}$ (2.0)	EtOAc	40	78
7	TBAB (10.0)	$TBHP^{dec}$ (2.0)	EtOAc	50	75
8	TBAB (10.0)	$TBHP^{aq}$ (2.0)	EtOAc	40	42
9	TBAB (10.0)	TBP (2.0)	EtOAc	40	23
10	TBAB (10.0)	$TBHP^{dec}$ (2.0)	CH_3CN	40	11
11	TBAB (10.0)	$TBHP^{dec}$ (2.0)	DCE	40	29
12	TBAB (10.0)	$TBHP^{dec}$ (2.0)	DCM	40	30
13	TBAB (10.0)	$TBHP^{dec}$ (2.0)	THF	40	6
14	TBAB (10.0)	$TBHP^{dec}$ (2.0)	*p*-dioxane	40	16
15	TBAB (10.0)	$TBHP^{dec}$ (2.0)	toluene	40	44
16	TBAB (10.0)	$TBHP^{dec}$ (2.0)	benzene	40	90
17	**TBAB (5.0)**	**$TBHP^{dec}$ (2.0)**	**benzene**	**40**	**91**
18	TBAB (2.5)	$TBHP^{dec}$ (2.0)	benzene	40	59
19	TBAB (20.0)	$TBHP^{dec}$ (2.0)	benzene	40	63
20	TBAB (5.0)	$TBHP^{dec}$ (1.0)	benzene	40	65
21	TBAB (5.0)	$TBHP^{dec}$ (3.0)	benzene	40	80
22[d]	TBAB (5.0)	$TBHP^{dec}$ (2.0)	benzene	40	79
23[e]	TBAB (5.0)	$TBHP^{dec}$ (2.0)	benzene	40	91

[a] *Reaction conditions:* benzoin (0.20 mmol), solvent (2.0 mL), 24 h, under air unless otherwise noted.
[b] Yields are determined by ^1H NMR with mesitylene as the internal standard.
[c] Reaction was carried out under N_2 atmosphere.
[d] Reaction was carried out for 20 h.
[e] Reaction was carried out for 30 h. cat. = catalyst, [Ox] = oxidant, Temp. = temperature, TEAB = tetraethylammonium bromide, TBAI = tetrabutylammonium iodide, TBAB = tetrabutylammonium bromide, $TBHP^{dec}$ = *tert*-butyl hydroperoxide (5.0–6.0 M in decane), TBP = *tert*-butyl peroxide, $TBHP^{aq}$ = *tert*-butyl hydroperoxide (70% aqueous solution), DCE = 1,2-dichloroethane, THF = tetrahydrofuran, DCM = dichloromethane.

tions (**2m–q**). It is worth noting that the protocol exhibits excellent compatibility towards tertiary alcohol (**2r**) as well, while it is totally inhibited by phenolic benzyl alcohol (**2s**) or aliphatic alcohol (**2t**).

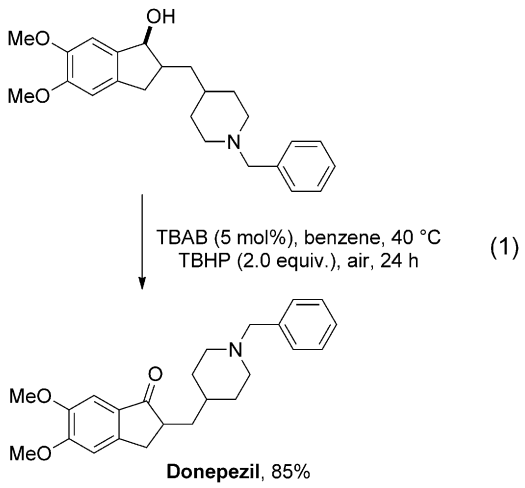
Further testing of this organocatalytic oxidation protocol revealed a similar broad substrate scope for diverse primary benzylic alcohols, albeit with slightly lower catalytic efficiency (Scheme 4). The reactions displayed remarkable functional group compatibility similar to that observed with secondary alcohols, including tolerance of catalytically reactive halogens (**2u, v**, **2y-b′**), nitrile (**2w**), nitro (**2x**), alkyl (**2c′**) as well as sulfur heterocycle (**2e′**). Once again, substrate electronic (*cf.* **2u–w**, **2c′**, **d′**) and steric effects (*cf.* 2**y-b′**) also resembled those observed with secondary alcohols.

As noted above, selective oxidation of unprotected polyols remains very limited especially with organocatalysts (mainly with TEMPO as the organocatalyst).[20] Hence, diols that exhibit specific selectivity challenges were explored under the standard reaction conditions to examine the chemoselectivity of our TBAB-based organocatalytic system (Scheme 5). Inspiringly, all the examined diols with both benzylic and aliphatic alcohols underwent selective oxidation efficiently, with nearly exclusive oxidation of 2° benzylic alcohol over 2°/1° aliphatic alcohols (*cf.* **2f′–2h′**). In a competition between 2° and 1° benzylic alcohol in a more challenging substrate, 4-(1-hydroxyethyl)benzyl alcohol, selective oxidation at the 2° benzylic alcohol position was observed as the major reaction and the product was isolated in about 70% yield, albeit oxidations at 1° benzylic or both 1° and 2° benzylic positions were also observed (*cf.* **2i′a–2i′c**). These observations indicate that our TBAB organocatalyst system appears to be more beneficial to the oxidation of the 2° benzylic alcohol in 4-(1-hydroxyethyl)benzyl alcohol. The potential application of this TBAB/TBHP catalytic



Scheme 3. TBAB-catalyzed oxidation of secondary benzylic/allylic alcohols. *General reaction conditions:* **1** (0.20 mmol), TBAB (5 mol%), TBHP (5.0–6.0 M in decane, 2.0 equiv.), benzene (2.0 mL), 40 °C, 24 h, under air. Isolated yields are given.

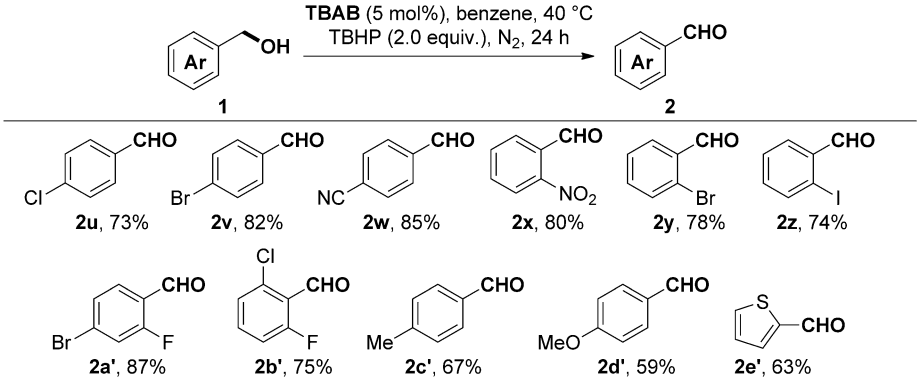
system was also explored and undoubtedly it is readily applicable for the construction of acetophenone fragments in biologically active drugs such as *Donepezil* (mainly used in the palliative treatment of Alzheimer's disease under the brandname *Aricept*) [Eq. (1)].



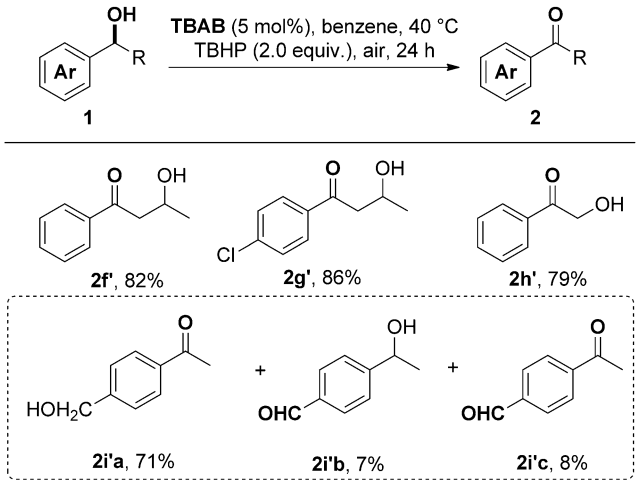
When investigating the reaction mechanism for this TBAB-catalyzed alcohol oxidation, the radical process is a preferred consideration. Therefore, a radical-trapping experiment was carried out. When TEMPO was introduced into the standard reaction conditions, the desired reaction almost completely did not occur (Scheme 6), thus indicating that this transformation is most likely to involve a radical intermediate.

On the basis of the above investigation and previous work,[21–23] a tentative mechanism for this organocatalytic alcohol oxidation is depicted in Scheme 7. Initially, *t*-BuO$^{\bullet}$ could be generated from TBHP with the assistance of TBAB.[21] This radical subsequently abstracts an α-hydrogen atom from benzylic alcohol,[22] and the resulting key intermediate α-hydroxybenzyl radical **A** is then further oxidized to the corresponding carbonyl product. The oxidation of **A** might occur through a SET process forming the intermediate α-hydroxybenzyl cation **B** directly[23] (the oxidation of **A** with TBHP to α-hydroxybenzyl cation **B** or the deprotonation of **A** with TBHP to radical anion could not be ruled out).

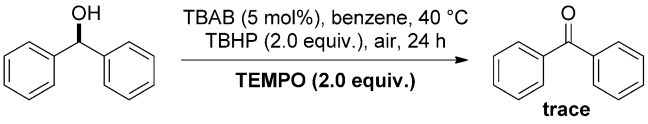
In summary, we have developed a simple but highly efficient catalytic system for alcohol oxidation with TBAB as the organocatalyst. This protocol facilitates a broad range of benzylic/allylic alcohols with excellent compatibility towards a variety of catalytically reactive groups such as alkyl, halide, nitrile, alkenyl,



Scheme 4. TBAB-catalyzed highly selective oxidation of primary benzylic alcohols. *General reaction conditions:* **1** (0.20 mmol), TBAB (5 mol%), TBHP (5.0–6.0 M in decane, 2.0 equiv.), benzene (2.0 mL), 40 °C, 24 h, under N_2. Isolated yields are given.

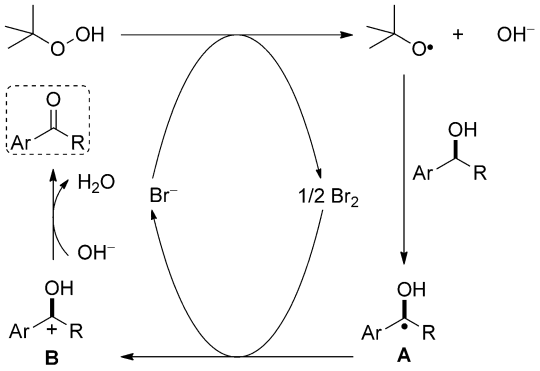


Scheme 5. TBAB-catalyzed highly selective oxidation of unprotected diols. *General reaction conditions:* **1** (0.20 mmol), TBAB (5 mol%), TBHP (5.0–6.0 M in decane, 2.0 equiv.), benzene (2.0 mL), 40 °C, 24 h, under air. Isolated yields are given.



Scheme 6. Investigation into the reaction mechanism.

heterocycles as well as aliphatic alcohols. Besides, it shows a preferential oxidation of 2° benzylic alcohol over 1° benzylic alcohol sites in 4-(1-hydroxyethyl)-benzyl alcohol. Thus, the simplicity, high efficiency, chemoselectivity and mildness of reaction conditions associated with this organocatalytic system suggest its potential for widespread use in synthetic chemistry. Further investigations on selective oxidations of various polyols and the catalytic mechanism are currently underway in our lab.



Scheme 7. Proposed mechanism.

Experimental Section

General Procedure

An oven-dried reaction vessel was charged with alcohol (0.20 mmol), tetra-*n*-butylammonium bromide (TBAB, 0.01 mmol, 5 mol%), benzene (2.0 mL, dried with 4 Å molecular sieves), and *tert*-butyl hydroperoxide (TBHP, 5.0–6.0 M in decane, 0.40 mmol) sequentially. Then the reaction vessel was sealed, placed into an oil bath and heated to 40 °C. After 24 h, the resulting mixture was cooled to room temperature, filtered through a short silica gel pad and washed with ethyl acetate. The above solution was evaporated under vacuum, and the residue was purified on a silica gel column with petroleum ether/ethyl acetate as the eluent to give the analytically pure carbonyl compounds **2a–2i′c**.

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