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DDQ/*tert*-Butyl nitrite-catalyzed aerobic oxidation of diarylmethane sp^3 C–H bonds

Jiaqi Ma [a], Zhiming Hu [a], Meichao Li [a], Weijuan Zhao [b], Xinquan Hu [a,c], Weimin Mo [a], Baoxiang Hu [a], Nan Sun [a], Zhenlu Shen [a,*]

[a] College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, PR China
[b] Zhejiang Research Institute of Chemical Industry, Ltd., Hangzhou 310023, PR China
[c] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

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ABSTRACT

An efficient 2,3-dichloro-5,6-dicyano-1,4-benzoquinone/*tert*-butyl nitrite-catalyzed aerobic oxidation of diarylmethane sp^3 C–H bonds in the presence of acetic acid has been developed. Under the optimal reaction conditions, a number of diarylmethanes can be directly converted to their corresponding diarylketones in good to excellent yields. In addition, a plausible reaction mechanism has been investigated.

1. Introduction

It is well known that diarylketones are an important class of organic molecules which can serve as structural motifs in functional molecules,[1] drugs[2] and advanced materials.[3] They are also useful precursors in the syntheses of various pharmaceutical compounds.[4] The traditional methods for synthesis of diarylketones include Friedel–Crafts acylation of aromatic compounds,[5] transition metal-catalyzed coupling reaction[6] and CO insertion reactions.[7] However, hash reaction conditions, toxic or expensive metal catalysts are still involved. In addition, a lot of methods that direct oxidation of diarylmethane sp^3 C–H bonds to prepare diarylketones employing different oxidants, such as $KBrO_3$, *N*-hydroxyphthalimide (NHPI), *tert*-butyl hydroperoxide (TBHP), H_2O_2, Oxone and oxygen, have been reported.[8] While metal catalysts were usually needed in these transformations. Xiong et al. described a metal-free catalytic oxidation system bromosuccinimide (NBS)-H_2O-air for preparing diversely functionalized diarylketones from diarylmethanes. It should be noted that the usage amount of NBS is large (5.0 equiv).[9] Another metal-free catalytic system I_2-Py-TBHP was reported by Wang et al., but stoichiometric amount oxidant TBHP was needed.[10] NHPI-catalyzed aerobic oxidation of benzylic derivatives has also been developed for synthesis of diarylketones, however low selectivities to products were still inevitable.[11] Developing a new metal-free aerobic oxidation catalytic system for oxidation of diarylmethane sp^3 C–H bonds to prepare diarylketones is still full of significance.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a well-known oxidant, and it has been successfully applied as the stoichiometric oxidant in a number of organic transformations. Recently, we had developed an efficient transition metal-free aerobic oxidation system DDQ/*tert*-butyl nitrite (TBN) and successfully applied it in benzyl alcohol oxidation and oxidative deprotection of benzyl-type ethers (including *p*-methoxybenzyl, *p*-phenylbenzyl, and benzyl ethers) in high selectivities.[12] The roles of DDQ, TBN and oxygen in the oxidation reaction have been discussed and studied in our previous research.[12,13] That is, DDQ acted as a catalyst, TBN was an efficient NO equivalent which was used to activate molecular oxygen,[14] and molecular oxygen served as the terminal oxidant. Cross-dehydrogenative coupling (CDC) reactions are a powerful tool for the construction of C–C and C–heteroatom bonds,[15] and many of CDC reactions can be promoted by stoichiometric DDQ or catalytic amount of DDQ with other oxidants.[16] Lei et al. described an example of CDC reaction between benzylic (not adjacent to heteroatoms or double bonds) sp^3 C–H bonds and carboxylic acids O–H bonds.[17] In their reaction system, 20 mol %

* Corresponding author. Tel.: +86 571 88320416; fax: +86 571 88320103; e-mail address: zhenlushen@zjut.edu.cn (Z. Shen).

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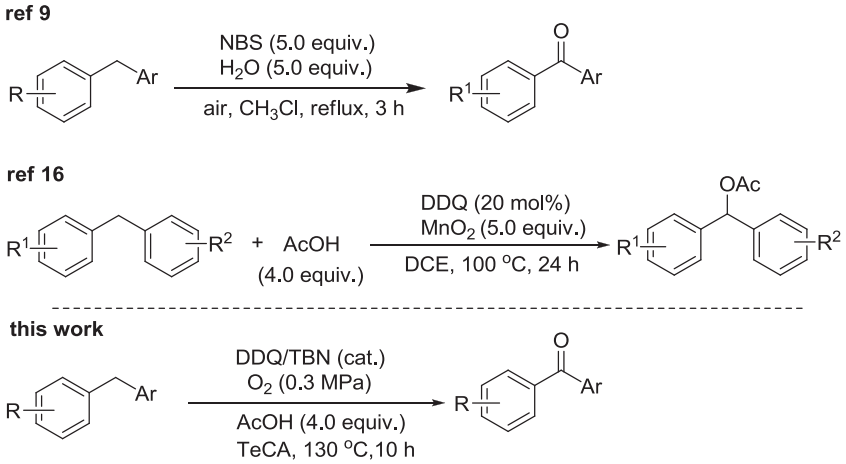
0040-4020/



Scheme 1. Transformation of diarylmethanes into diarylketones.

DDQ with a large excess of metal oxidant MnO_2 (5.0 equiv) were employed. We initially attempted to use our previous DDQ/TBN/O_2 system to instead of DDQ/MnO_2 system in this CDC reaction. When the CDC reaction of diphenylmethane and acetic acid was performed with the combination of catalytic amounts of DDQ and TBN under atmospheric pressure of O_2 in chlorobenzene, it was found that benzhydryl acetate was accompanied by about 10% of benzophenone. Thus, we envisioned to develop a new general methodology for the direct synthesis of diarylketones from diarylmethanes.

Herein, we report a DDQ/TBN-catalyzed aerobic oxidation of diarylmethanes sp^3 C–H Bonds in the presence of acetic acid and discuss a possible reaction mechanism (Scheme 1). To the best of our knowledge, this work is the first example of direct transformation of diarylmethanes to their corresponding diarylketones catalyzed by DDQ/TBN with molecular oxygen as the oxidant.

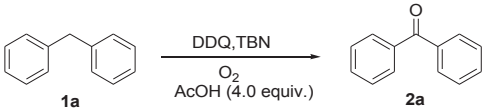
2. Results and discussion

Initially, we started to optimize the reaction conditions with diphenylmethane (**1a**) as the model substrate (Table 1). To establish the optimal reaction conditions, a range of solvents were tested. Among the screened solvents, **1a** could be oxidized to carbonylation product benzophenone (**2a**) in 82% conversion and 94% selectivity in 1,1,2,2-tetrachloroethane(TeCA) within 5 h at 130 °C in the presence of 4.0 equiv of AcOH (entry 7). In other tested solvents such as PhCl, 1,2-dichlorobenzene and AcOH, CDC reaction between diphenylmethane benzylic sp^3 C–H bond and acetic acid O–H bond was observed and a large amount of benzhydryl acetate was generated (entries 1, 4 and 5). The reaction did not proceed as efficiently in ethylene glycol diethyl ether and dioxane (entries 3 and 6). In toluene, 44% conversion of **1a** was obtained, but the selectivity to **2a** was only 5% (entry 2). The reaction results in the nonpolar solvents containing chlorine were better than that in other solvents. It may be due to that the boiling points of these chlorinated solvents were higher than reaction temperature of 130 °C, while others were lower than 130 °C. Encouraged by the results in the solvent of TeCA, the oxygen pressure and the reaction temperature were also tested. Entries 7–11 illustrate the impact of oxygen pressure and reaction temperature on the efficiency of this reaction. Reducing the oxygen pressure from 0.3 MPa to 0.2 MPa led to a lower selectivity to **2a** (entries 7 and 8). Increasing the reaction temperature from 110 °C to 130 °C led to a higher conversion of **1a** (entries 9–11), thus 130 °C was chosen as the optimal reaction temperature.

Later on, the loads of DDQ, TBN and AcOH were also attempted to be reduced. When the load of TBN was reduced to 20 mol %, **1a** could also be fully converted to **2a** in 99% selectivity (entry 12). But decreasing the load of DDQ to 20 mol % led to a lower conversion and selectivity (entry 13). When the load of AcOH was reduced to 2.0 equiv, conversion of **1a** was decreased to 88% (entry 14). After detailed exploration of the reaction conditions with diphenylmethane as the substrate, we chose 30 mol % DDQ and 20 mol % TBN in the presence of 4.0 equiv of AcOH in TeCA at 130 °C under 0.3 MPa of O_2 as the optimal reaction conditions (entry 12).

Having gotten the optimal reaction conditions, a number of substituted diarylmethanes were investigated (Table 2). The data in Table 2 show the yields of diarylketones to be good to excellent. Most of the substituted diarylmethanes showed high reactivity affording the desired products. It is clear that the presence of meta-position or para-position methyl and methoxy substituents increased the reaction activity of **1c**–**1f** (entries 3–6), a short reaction time 5–8 h was enough compared with model substrate **1a** and the isolated yields of **2c**–**2f** were all higher than 96%. However,

Table 1
Optimization of DDQ/TBN-catalyzed aerobic oxidation of **1a**[a]

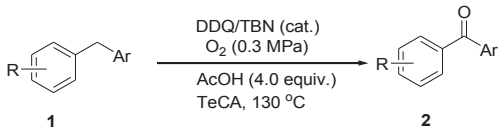


1a **2a**

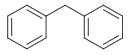
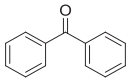
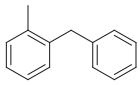
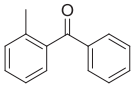
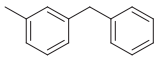
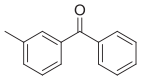
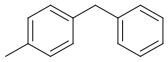
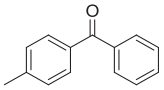
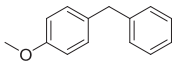
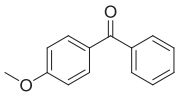
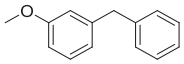
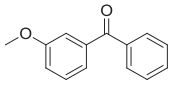
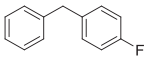
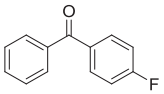
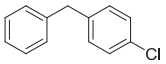
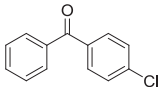
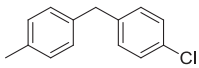
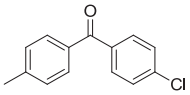
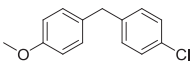
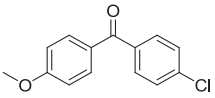
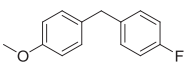
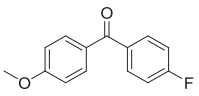
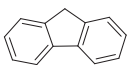
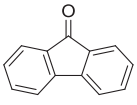
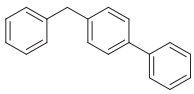
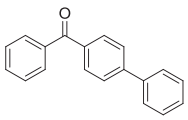
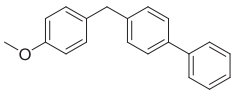
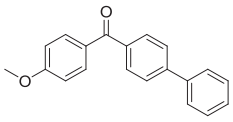
Entry	Solvent	DDQ (mol %)	TBN (mol %)	P(O_2) (MPa)	T[b] (°C)	Time (h)	Conv.[c] (%)	Select.[c] (%)
1	PhCl	30	30	0.3	130	5	56	57
2	Toluene	30	30	0.3	130	5	44	5
3	$EtO(CH_2)_2OEt$	30	30	0.3	130	5	<5	—
4	1,2-$C_6H_4Cl_2$	30	30	0.3	130	5	82	77
5	AcOH	30	30	0.3	130	5	44	12
6	Dioxane	30	30	0.3	130	5	<1	—
7	TeCA[e]	30	30	0.3	130	5	82	94
8	TeCA	30	30	0.2	130	5	84	83
9	TeCA	30	30	0.3	110	10	90	91
10	TeCA	30	30	0.3	120	10	97	98
11	TeCA	30	30	0.3	130	8	100	96
12	TeCA	30	20	0.3	130	10	100	99
13	TeCA	20	30	0.3	130	10	82	91
14[d]	TeCA	30	20	0.3	130	10	88	96

[a] Reaction conditions: **1a** (2 mmol), AcOH (8 mmol).
[b] Oil bath temperature.
[c] Determined by GC with area normalization method.
[d] AcOH (4 mmol).
[e] TeCA: 1,1,2,2-tetrachloroethane.

Table 2
Transformation of diarylmethanes into diarylketones[a]

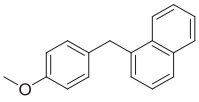
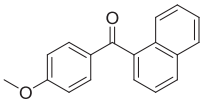
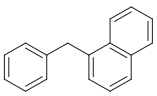
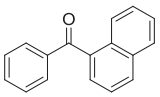
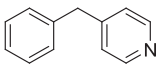
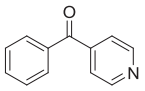
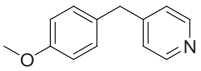
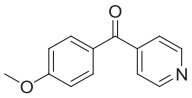
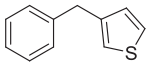
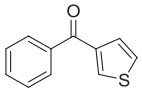


1 2

Entry	Substrate		Product		Time (h)	Conv.[b] (%)	Yield[c] (%)
1		**1a**		**2a**	10	100	97
2		**1b**		**2b**	12	92	89
3		**1c**		**2c**	8	100	96
4		**1d**		**2d**	8	100	97
5		**1e**		**2e**	5	100	98
6		**1f**		**2f**	5	100	97
7[d]		**1g**		**2g**	24	89	65
8[d]		**1h**		**2h**	24	81	65
9		**1i**		**2i**	12	100	99
10		**1j**		**2j**	12	100	99
11		**1k**		**2k**	12	100	96
12[e]		**1l**		**2l**	20	91	83
13		**1m**		**2m**	12	96	95
14[f]		**1n**		**2n**	12	100	96

(*continued on next page*)

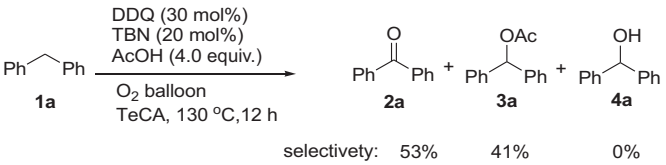
Table 2 (*continued*)

Entry	Substrate	Product	Time (h)	Conv.[b] (%)	Yield[c] (%)
15[f]	 **1o**	 **2o**	12	100	99
16	 **1p**	 **2p**	12	100	98
17[g]	 **1q**	 **2q**	12	100	99
18	 **1r**	 **2r**	12	100	90
19	 **1s**	 **2s**	10	100	99

[a] Reaction conditions: **1** (2 mmol), AcOH (8 mmol), DDQ (30 mol %), TBN (20 mol %), 1,1,2,2-tetrachloroethane (20 mL), 130 °C (oil bath), O_2 (0.3 MPa).
[b] Determined by GC with area normalization method.
[c] Isolated yield.
[d] AcOH (16 mmol), O_2 (0.5 MPa).
[e] O_2 (0.5 MPa).
[f] DDQ (20 mol %), TBN (20 mol %).
[g] 150 °C (oil bath).

sterically hindered substrate **1b** containing *o*-methyl showed lower reactivity (entry 2), a 92% conversion and 89% isolated yield could be obtained in 12 h. Notably, the reaction of substrates with electron-withdrawing substituents, for example, 1-benzyl-4-fluorobenzene (**1g**) and 1-benzyl-4-chlorobenzene (**1h**) required a longer reaction time (24 h) and a higher oxygen pressure (0.5 MPa), also more AcOH (8 equiv) was needed. The conversion of **1g** and **1h** were 89% and 81%, respectively. The isolated yields of the corresponding ketones **2g** and **2h** were only 65%, it was due to that CDC reaction products also existed with the desired ketones (entries 7 and 8). Interestingly, diarylmethanes bearing both electron-donating and electron-withdrawing substituents (**1i**–**1k**) were transformed smoothly, and quantitatively afforded their corresponding ketones in 96%–99% isolated yields (entries 9–11). When 9*H*-fluorene (**1l**) was used as the substrate, 91% conversion of **1l** and 83% isolated yield of 9*H*-fluoren-9-one (**2l**) were achieved in 20 h by increasing the oxygen pressure to 0.5 MPa (entry 12). Much to our delight, the para-position phenyl substrates **1m** and **1n**, polycyclic aromatic substrates **1o** and **1p**, were also converted to their corresponding products in excellent isolated yields (entries 13–16). In addition, less amount of DDQ (20 mol %) was enough in the reaction of **1n** and **1o** (entries 14 and 15). Heterocyclic substrates containing pyridine ring, **1q** and **1r**, were also tested, and they were almost fully converted into ketones **2q** and **2r** in 99% and 90% isolated yields (entries 17 and 18). According to Xiong et al., substrate containing a heterocyclic thiophene (**1s**) would converted into two Br-containing products (2,5-dibromothiophen-3-yl)(phenyl)methanone and (2,5-dibromothiophen-3-yl)(phenyl) methanol in 51% and 38% yields in the NBS-H_2O-Air system.[9] However, in this DDQ/TBN/O_2 system, the isolated yield of product **2s** could be obtained as high as 99%.

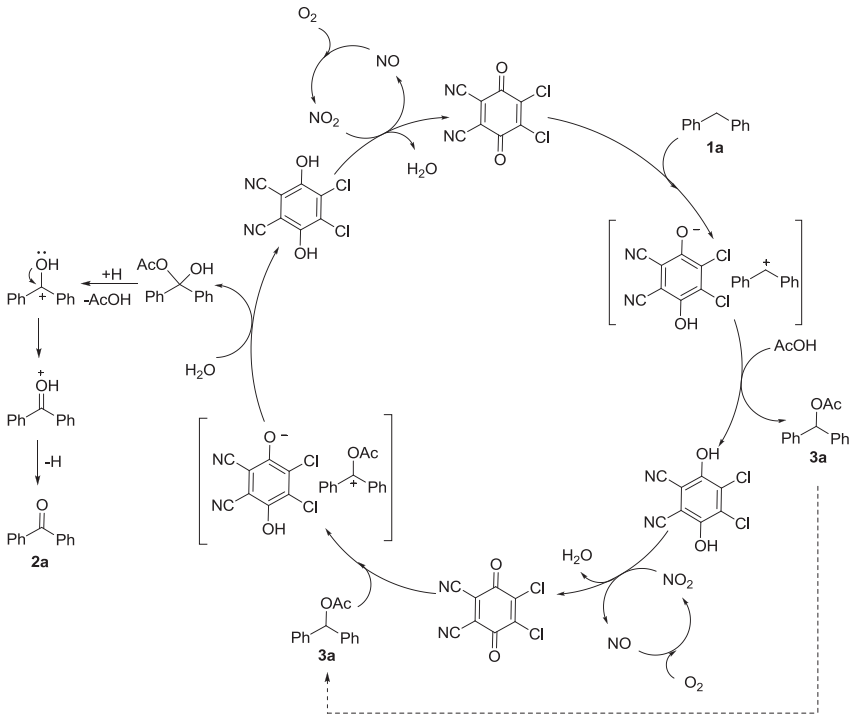
With these results in hand, we tried to explore the plausible reaction mechanism. When **1a** was treated with the condition of 30 mol % DDQ, 20 mol % TBN and 4.0 equiv of AcOH under atmospheric pressure of O_2 (Scheme 2), the selectivity of **2a** was only 53%, and 41% CDC reaction product **3a** was observed. However, diphenylmethanol (**4a**) could not be detected in the reaction mixture. If the solvent TeCA was further replaced by chlorobenzene, the selectivity to CDC reaction product **3a** was high to 82%. These results implied that **3a** was the intermediate product.



Scheme 2. DDQ/TBN-catalyzed aerobic oxidation of **1a** under atmospheric pressure of O_2.

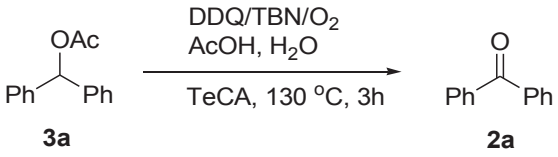
A plausible reaction mechanism for the aerobic oxidation of **1a** into **2a** with DDQ/TBN catalytic system in the presence of AcOH is shown in Scheme 3. The initial step is the benzylic CDC reaction promoted by DDQ, and **1a** is converted into **3a** in the presence of AcOH, which also has been reported.[16] Then **3a** can be further transformed to **2a** in the presence of DDQ and H_2O. As shown in Scheme 3, DDQ is essential in the reaction process from intermediate **3a** to product **2a** because benzylic hydrogen atom of **3a** should be removed by DDQ.

To verify the necessity of DDQ in the transformation of **3a** to **2a**, **3a** was synthesized and employed as the initial substrate (Table 3). The DDQ/TBN aerobic oxidation system will generate small amount of water in the stage of **3a** formation, thus 1.0 equiv of water was added in the transformation of **3a** to **2a**. As shown in Table 3, when DDQ was absent, **3a** could not be converted at all (entries 1 and 2).



Scheme 3. Plausible reaction mechanism.

Table 3
To verify the necessity of DDQ in the transformation **3a** to **2a**[a]

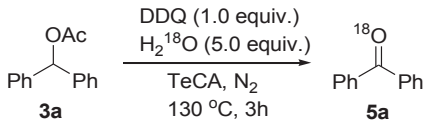


Entry	DDQ (mol %)	TBN (mol %)	AcOH (equiv)	H_2O (equiv)	Conv.[b] (%)	Select.[b] (%)
1	—	20	—	1	0	—
2	—	20	2	1	0	—
3	30	20	—	1	100	>99
4	30	20	2	1	100	>99

[a] Reaction conditions: **3a** (2 mmol), H_2O (2 mmol), TBN (20 mol %), TeCA (20 mL), 130 °C (oil bath), O_2 (0.3 MPa).
[b] Determined by GC with area normalization method.

In contrast to this, when DDQ was present in the reaction, **3a** could be fully converted to product **2a** easily in 3 h with or without AcOH (entries 3 and 4). These results suggest that DDQ is essential in the transformation of **3a** to **2a**.

To further confirm the mechanism, an isotope trace experiment was conducted with stoichiometric water (5.0 equiv) labeled with ^{18}O (Scheme 4). To eliminate the influence of water generated from DDQ/TBN aerobic oxidation system, stoichiometric DDQ (1.0 equiv) was employed under nitrogen atmosphere. In the solvent of dry TeCA for 3 h, the ^{18}O-labeled product **5a** confirmed by GC–MS was generated in 95% yield.[18] These experimental results indicate that the proposed mechanism is reasonable.



Scheme 4. The isotope trace experiment.

In conclusion, we have successfully applied the DDQ/TBN/O_2 system, a metal-free catalytic oxidation system, for the oxidation of diarylmethane sp^3 C–H bonds in the presence of acetic acid. Under the optimal reaction conditions, a variety of diarylmethanes can be converted to their corresponding diarylketones in good to excellent yields and selectivities. A plausible reaction mechanism has been investigated by control experiments and isotope trace experiment. This method is environmentally benign and would facilitate the syntheses of diarylketones with electron-donating substituents especially.

3. Experimental section

3.1. General

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained on a Bruker Avance III spectrometer. $CDCl_3$ was used as the solvent with tetramethylsilane (TMS) as the internal standard. GC analyses were conducted on an Agilent GC7890N system with a flame ionization detector (FID) and a SE-54 or OV-17 capillary column. GC–MS was performed on Thermo Trace ISQ instrument with TG 5MS capillary column. Melting points were measured using XRL-1 melting point instrument and uncorrected. Diarylmethanes **1a**–**1s** and benzhydryl acetate **3a** were prepared in our laboratory. Other reagents were purchased from supplier and used without any further treatment.

3.2. A typical procedure for DDQ/TBN-catalyzed aerobic oxidation of diarylmethanes

A Teflon-lines 316 L stainless steel autoclave (300 mL) equipped with magnetic stirring bar was charged with substituted diarylmethanes **1** (2 mmol), 136.2 mg DDQ (0.6 mmol, 30 mol %), 41.2 mg TBN (0.4 mmol, 20 mol %), 480 mg acetic acid (8 mmol) and 20 mL TeCA. The autoclave was closed and charged with oxygen to 0.3 MPa. Then the autoclave was placed in an oil bath, which was preheated to 130 °C. The mixture was then stirred for a certain time

until the reaction was completed. The autoclave was taken out from the oil bath, cooled to room temperature and carefully depressurized. The mixture was concentrated under reduced pressure and purified by column chromatography to give the desired diarylketones.

*3.2.1. Benzophenone (**2a**).*[8d,9] White solid; mp: 48–49 °C (lit.[19] 46–47.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.80 (m, 4H), 7.61–7.58 (m, 2H), 7.50–7.47 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 137.6, 132.4, 130.1, 128.3; MS (EI), *m*/*z* 182.10 [M^+, 36%], 105.06 (100%), calcd for $C_{13}H_{10}O$=182.07.

*3.2.2. Phenyl(o-tolyl)methanone (**2b**).*[6a] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.61–7.59 (m, 1H), 7.49–7.46 (m, 2H), 7.43–7.40 (m, 1H), 7.34–7.25 (m, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 138.6, 137.8, 136.7, 133.1, 131.0, 130.3, 130.1, 128.52, 128.48, 125.2, 20.0; MS (EI), *m*/*z* 196.10 [M^+, 70%], 195.01 (100%), calcd for $C_{14}H_{12}O$=196.09.

*3.2.3. Phenyl(m-tolyl)methanone (**2c**).*[6a] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.65 (s, 1H), 7.62–7.59 (m, 2H), 7.51–7.48 (m, 2H), 7.43–7.36 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 138.2, 137.8, 137.7, 133.2, 132.4, 130.5, 130.0, 128.3, 128.1, 127.4, 21.4; MS (EI), *m*/*z* 196.13 [M^+, 60%], 119.01 (100%), calcd for $C_{14}H_{12}O$=196.09.

*3.2.4. Phenyl(p-tolyl)methanone (**2d**).*[6a,9] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.74 (d, *J*=8.2 Hz, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 7.31–7.28 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.5, 143.2, 138.0, 134.9, 132.2, 130.3, 129.9, 129.0, 128.2, 21.6; MS (EI), *m*/*z* 196.09 [M^+, 45%], 119.00 (100%), calcd for $C_{14}H_{12}O$=196.09.

*3.2.5. (4-Methoxyphenyl)(phenyl)methanone (**2e**).*[5a,5b] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86–7.83 (m, 2H), 7.78–7.76 (m, 2H), 7.60–7.57 (m, 1H), 7.50–7.47 (m, 2H), 7.00–6.97 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 163.2, 138.3, 132.5, 131.9, 130.2, 129.7, 128.2, 113.6, 55.5; MS (EI), *m*/*z* 212.11 [M^+, 38%], 134.96 (100%), calcd for $C_{14}H_{12}O_2$=212.08.

*3.2.6. (3-Methoxyphenyl)(phenyl)methanone (**2f**).*[6e] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.82 (m, 2H), 7.62–7.59 (m, 1H), 7.51–7.48 (m, 2H), 7.41–7.35 (m, 3H), 7.15–7.14 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 159.6, 138.9, 137.6, 132.4, 130.0, 129.2, 128.3, 122.8, 118.8, 114.4, 55.4; MS (EI), *m*/*z* 212.12 [M^+, 82%], 105.00 (100%), calcd for $C_{14}H_{12}O_2$=212.08.

*3.2.7. (4-Fluorophenyl)(phenyl)methanone (**2g**).*[6a,9] White solid; mp: 94–95 °C (lit.[20] 45–47 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.77 (m, 4H), 7.62–7.60 (m, 1H), 7.52–7.47 (m, 4H); ^{13}C NMR (125 MHz, CD_3Cl_3) δ 195.2, 165.4 (d, *J*=252.4 Hz), 137.5, 133.8 (d, *J*=3.3 Hz), 132.7 (d, *J*=9.1 Hz), 132.5, 129.9, 128.4, 115.4 (d, *J*=21.8 Hz); MS (EI), *m*/*z* 199.93 [M^+, 83%], 123.07 (100%), calcd for $C_{13}H_9FO$=200.06.

*3.2.8. (4-Chlorophenyl)(phenyl)methanone (**2h**).*[6a,9,21] White solid; mp: 72–73 °C (lit.[20] 74–76 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.75 (m, 4H), 7.62–7.59 (m, 1H), 7.51–7.46 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 138.9, 137.3, 135.9, 132.6, 131.5, 129.9, 128.6, 128.4; MS (EI), *m*/*z* 216.07 [M^+, 50%], 105.04 (100%), calcd for $C_{13}H_9ClO$=216.03.

*3.2.9. (4-Chlorophenyl)(p-tolyl)methanone (**2i**).*[22] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.71 (d, *J*=8.1 Hz, 2H), 7.48–7.46 (m, 2H), 7.31 (d, *J*=8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 143.6, 138.7, 136.3, 134.6, 131.4, 130.2, 129.2, 128.6, 21.7; MS (EI), *m*/*z* 229.91 [M^+, 28%], 119.05 (100%), calcd for $C_{14}H_{11}ClO$=230.05.

*3.2.10. (4-Chlorophenyl)(4-methoxyphenyl)methanone (**2j**).*[22] White solid; mp: 124–125 °C (lit.[20] 116–118 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.80 (m, 4H), 7.17 (t, *J*=8.7 Hz, 2H), 7.00–6.98 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.3, 163.4, 138.3, 136.6, 132.4, 131.1, 129.8, 128.5, 113.7, 55.5; MS (EI), *m*/*z* 246.02 [M^+, 25%], 135.05 (100%), calcd for $C_{14}H_{11}ClO_2$=246.04.

*3.2.11. (4-Fluorophenyl)(4-methoxyphenyl)methanone (**2k**).*[21] White solid; mp: 94–95 °C (lit.[20] 89–91 °C);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82–7.81 (m, 2H), 7.73–7.71 (m, 2H), 7.48–7.46 (m, 2H), 7.00–6.98 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.1, 165.1 (d, *J*=251.6 Hz), 163.3, 134.5 (d, *J*=2.6 Hz), 132.5, 132.3 (d, *J*=9.1 Hz), 130.1, 115.4 (d, *J*=21.7 Hz), 113.7, 55.6; MS (EI), *m*/*z* 230.06 [M^+, 35%], 135.05 (100%), calcd for $C_{14}H_{11}FO_2$=230.07.

*3.2.12. 9H-Fluoren-9-one (**2l**).*[8c,8d,11b] White solid; mp: 83–84 °C (lit.[19] 79–82 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J*=7.4 Hz, 2H), 7.48–7.43 (m, 4H), 7.28–7.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 144.4, 134.6, 134.1, 129.0, 124.2, 120.2. MS (EI), *m*/*z* 179.98 [M^+, 100%], calcd for $C_{13}H_8O$=180.06.

*3.2.13. Biphenyl-4-yl(phenyl)methanone (**2m**).*[10] White solid; mp: 100–101 °C (lit.[23] 98–99 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2H), 7.87–7.85 (m, 2H), 7.74–7.72 (m, 2H), 7.68–7.66 (m, 2H), 7.64–7.61 (m, 1H), 7.54–7.49 (m, 4H), 7.45–7.41 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 145.3, 140.1, 137.9, 136.3, 132.4, 130.8, 130.1, 129.0, 128.4, 128.2, 127.4, 127.0; MS (EI), *m*/*z* 258.08 [M^+, 70%], 181.00 (100%), calcd for $C_{19}H_{14}O$=258.10.

*3.2.14. Biphenyl-4-yl(4-methoxyphenyl)methanone (**2n**).*[24] White solid; mp: 87–88 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.86 (m, 4H), 7.73–7.71 (m, 2H), 7.68–7.66 (m, 2H), 7.52–7.49 (m, 2H), 7.44–7.42 (m, 1H), 7.02–7.00 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 163.2, 144.7, 140.1, 136.9, 132.5, 130.4, 130.3, 128.9, 128.1, 127.3, 126.9, 113.6, 55.5; MS (EI), *m*/*z* 288.06 [M^+, 40%], 135.02 (100%), calcd for $C_{20}H_{16}O_2$=288.12.

*3.2.15. (4-Methoxyphenyl)(naphthalen-1-yl)methanone (**2o**).*[25] White solid; mp: 94–95 °C (lit.[26] 97 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02–7.86 (m, 5H), 7.58–7.48 (m, 4H), 6.95–6.94 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 163.9, 137.1, 133.7, 132.8, 131.1, 130.9, 130.7, 128.4, 127.1, 126.9, 126.4, 125.7, 124.5, 113.8, 55.5; MS (EI), *m*/*z* 262.14 [M^+, 70%], 135.04 (100%), calcd for $C_{18}H_{14}O_2$=262.10.

*3.2.16. Naphthalen-1-yl(phenyl)methanone (**2p**).*[6a,10] White solid; mp: 72–73 °C (lit.[10] 75–76 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J*=8.2 Hz, 1H), 8.03 (d, *J*=8.2 Hz, 1H), 7.96–7.94 (m, 1H), 7.90–7.88 (m, 2H), 7.64–7.28 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 138.3, 136.4, 133.7, 133.2, 131.3, 131.0, 130.4, 128.45, 128.41, 127.8, 127.3, 126.5, 125.7, 124.3; MS (EI), *m*/*z* 232.12 [100%], calcd for $C_{17}H_{12}O$=232.09.

*3.2.17. Phenyl(pyridin-4-yl)methanone (**2q**).*[27] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84–8.83 (m, 2H), 7.85–7.83 (m, 2H), 7.69–7.65 (m, 1H), 7.61–7.60 (m, 2H), 7.55–7.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 150.4, 144.4, 136.0, 133.6, 130.2, 128.7, 122.9; MS (EI), *m*/*z* 183.07 [M^+, 40%], 105.07 (100%), calcd for $C_{12}H_9NO$=183.07.

*3.2.18. (4-Methoxyphenyl)(pyridin-4-yl)methanone (**2r**).*[24] Brown solid; mp: 119–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J*=3.9 Hz, 2H), 7.84 (d, *J*=8.9 Hz, 2H), 7.56 (d, *J*=5.7 Hz, 2H), 7.00 (d,

J=8.9 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 164.1, 150.1, 145.5, 132.7, 128.7, 122.9, 114.0, 55.7; MS (EI), m/z 212.99 [M^+, 33%], 135.09 (100%), calcd for $C_{13}H_{11}NO_2$=213.08.

*3.2.19. Phenyl(thiophen-3-yl)methanone (**2s**).*[28] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96–7.95 (m, 1H), 7.87–7.86 (m, 2H), 7.63–7.59 (m, 2H), 7.52–7.49 (m, 2H), 7.41–7.40 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.0, 141.3, 138.6, 133.9, 132.3, 129.4, 128.6, 128.4, 126.2; MS (EI), m/z 187.90 [M^+, 60%], 110.98 (100%), calcd for $C_{11}H_8OS$=188.03.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.07.042.

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