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DTBP-mediated cross-dehydrogenative coupling of 3-aryl benzofuran-2(3*H*)-ones with toluenes/phenols for all-carbon quaternary centers†

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We have developed a transition-metal free protocol for efficient cross-dehydrogenative coupling of 3-aryl benzofuran-2(3*H*)-ones and toluenes/phenols using DTBP as an oxidant. A diverse range of 3-aryl benzofuran-2(3*H*)-ones, toluenes, and phenols undergo C–H bond cleavage to generate all-carbon quaternary centers in good yields, making this protocol useful for the synthesis of complex molecules. A gram scale experiment was performed in good yield.

Introduction

Cross-dehydrogenative coupling (CDC) is a straightforward strategy for carbon–carbon bond formation.¹ Many pioneering efforts have been made to develop CDC methodologies to access useful motifs by using a variety of transition metal catalysts.² As for the transition-metal free methods for CDC reactions, there are only a few pioneering works that have been developed,³ including oxidative promotion, photocatalysis and electrochemical catalysis. Although a transition-metal free CDC reaction has been developed, its application in all-carbon quaternary center construction has never been disclosed.⁴

All-carbon quaternary centers are broadly present in various bioactive natural products, artificially synthesized pharmaceutical and medicinal molecules,⁵ such as hopeahainol A,^{5b} oxyphenisatin, TOP216 analogue,^{5c} yuccaol,^{5d} estrogen receptor modulator,^{5e} cyclophilin inhibitor,^{5f} hamigeran B (Fig. 1).^{5g} These molecules show unique bioactivities due to the rigid three-dimensional structure. Therefore, the efficient and selective construction of all-carbon quaternary stereocenters has received intensive attention in recent decades.⁶ However, the construction of quaternary carbon centers *via* CDC reaction is rare.⁷ Previously, we have developed a Cu-catalyzed CDC reaction of 3-aryl benzofuranones with heteroatom arenes, which furnishes highly functionalized 3,3-diaryl benzofuranones bearing a three aryls quaternary carbon center at C3 position in good yields.⁷¹ These complex compounds can be

decarbonylation to be triaryl methane easily.⁸ However, this protocol can be only applied to the coupling between C(sp³)-H bond and C(sp²)-H bond.

Herein, we disclosed the first example of the construction of all-carbon quaternary centers *via* a transition-metal free CDC reaction of 3-aryl benzofuran-2(3*H*)-ones with toluenes/phenols by using DTBP (di-*t*-butyl peroxide) as an oxidant, which the two different C(sp³)-H bonds can be cross-coupling site-selectively in good yields. This protocol shows a broad substrate scope and gram-scalable ability. While toluenes were changed into phenols with methyl group in this protocol, the *ortho*-C(sp²)-H bond of phenol was activated site selectively.

Results and discussion

Initially, we explored the reactions using 4-methylbenzofuranone (1a) and toluene (2a) as substrates under different reaction conditions (Table 1). CuI, NiCl₂, and CoCl₂ were then

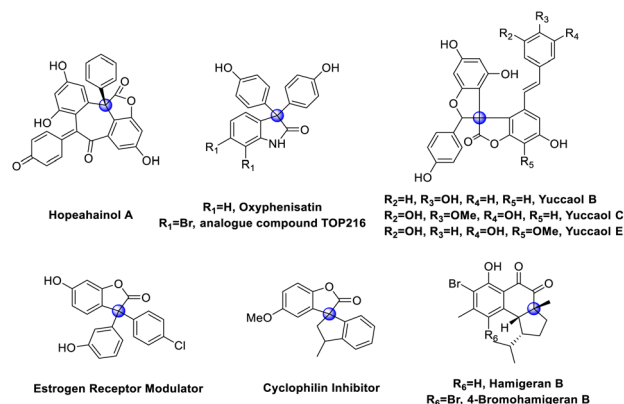


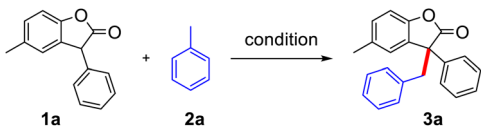
Fig. 1 Bioactive all-carbon quaternary centers.

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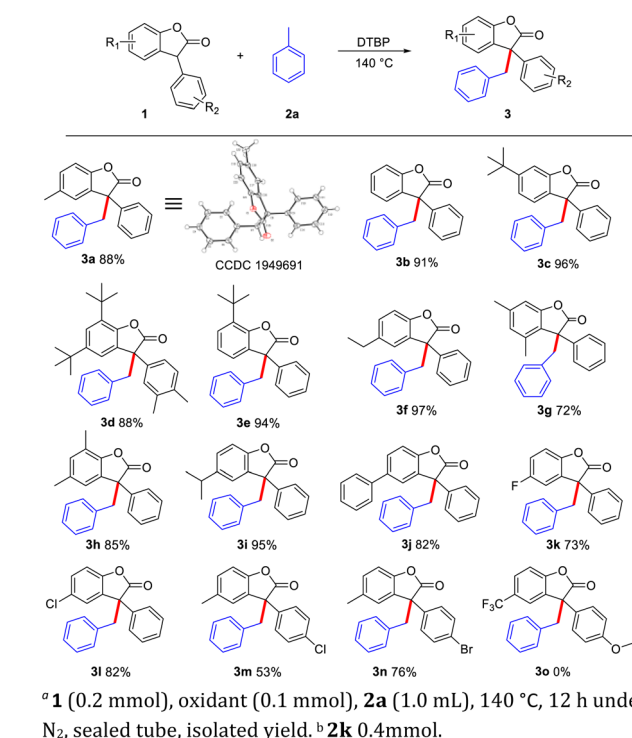
Table 1 Survey on condition for 2a formation^a

					
Entry	Cat. (mol%)	Oxidant	Solvent	Temp. (°C)	Yield ^a (%)
1	CuI (10)	DTBP	Toluene	140	83
2	NiCl ₂ (10)	DTBP	Toluene	140	88
3	CoCl ₂ (10)	DTBP	Toluene	140	88
4	NiCl ₂ (5)	DTBP	Toluene	140	86
5	NiCl ₂ (20)	DTBP	Toluene	140	45
6	—	DTBP	Toluene	140	88
7 ^b	—	DTBP	Toluene	140	77
8	—	TBHP	Toluene	140	10
9	—	CHP	Toluene	140	27
10	—	mCPBA	Toluene	140	0
11	—	DTBP	Toluene/DMF	140	0
12	—	DTBP	Toluene/DMSO	140	0
13 ^c	—	DTBP	Toluene	140	12
14 ^d	—	DTBP	Toluene	140	50
15	—	DTBP	Toluene	160	87
16	—	DTBP	Toluene	120	32

^a Reaction conditions: **1a** (0.2 mmol), cat. (mol%), oxidant (0.1 mmol) and **2a** (1.0 mL), 12 h, under N₂, sealed tube, isolated yield. ^b Under air. ^c DTBP 0.2 equiv. ^d DTBP 1.0 equiv. TBHP = *t*-butylhydroperoxide, CHP = cumyl hydroperoxide, mCPBA = *meta*-chloroperoxybenzoic acid, DMF = *N,N*-dimethyl-formicaci, DMSO = dimethyl sulfoxide.

examined in the presence of DTBP as an oxidant under N₂ atmosphere, the yields of **3a** were 83%, 88%, 88%, respectively (entries 1–3) and changed the amount of catalyst resulting in a decrease of yield (entries 4–5). However, without a metal catalyst, the yield of **3a** was also up to 88% (entry 6), indicating only DTBP is enough for this protocol. While the reaction atmosphere was changed into the air, the yield of **3a** was decreased to 77% (entry 7). When DTBP was replaced by TBHP, CHP and mCPBA resulted in the decrease of the yield of **3a** to 10%, 27% and no product (entry 8–10). When mixed solvent was added, the target product could not be obtained (entry 11–12). Both increasing and decreasing the amount of oxidant would have a negative impact on the reaction (entry 13–14). The adoption of other temperatures also resulted in lower yields (entries 15–16). The molecular structure of **3a** were being isolated as racemic mixtures and has been unambiguously confirmed by single crystal X-ray diffraction study (figure in Scheme 1, CCDC 1949691†).

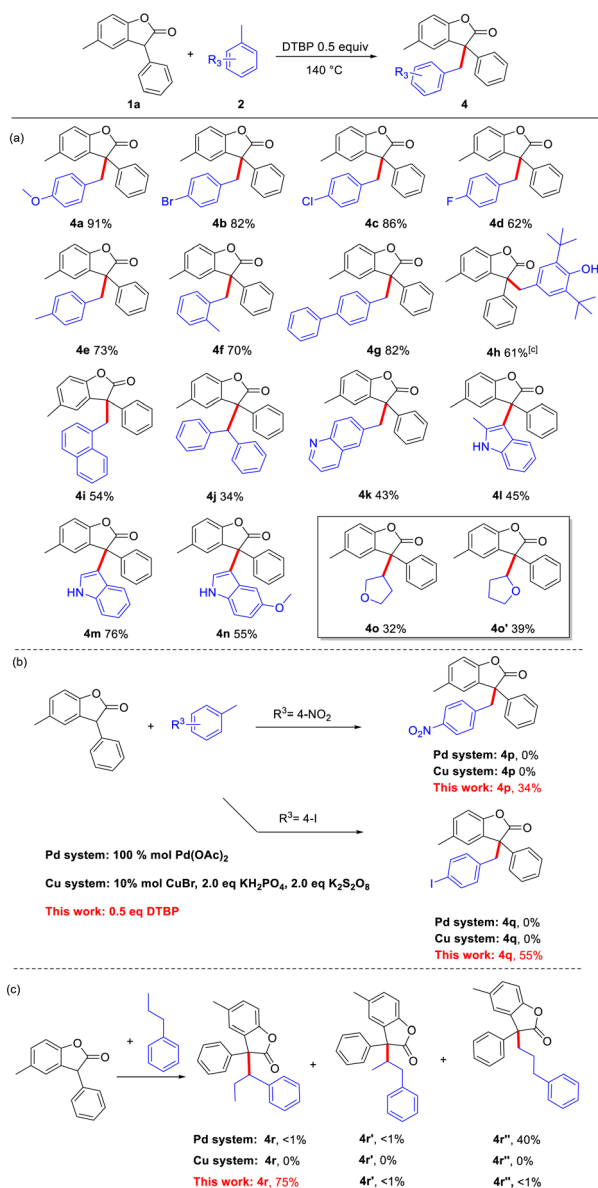
With the optimized reaction conditions in hand, we next investigated the substrate scope (Scheme 1). A variety of substituted benzofuranones (**1**) could proceed well in this CDC reaction to deliver corresponding products in moderate to good yields, and valuable groups such as 4-H (**3b**, 91%), 3-*tert*-butyl (**3c**, 96%), 2,4-di-*tert*-butyl (**3d**, 88%), 2-*tert*-butyl (**3e**, 94%), 4-ethyl (**3f**, 97%), 3,5-dimethyl (**3g**, 72%), 2,4-dimethyl (**3h**, 85%), 4-isopropyl (**3i**, 95%), 4-phenyl (**3j**, 82%), 4-fluorine (**3k**, 73%), 4-chloro (**3l**, 82%, **3m**, 53%), and 4-bromo (**3n**, 76%) were tolerated. Overall, the adaptability of the reaction system to

Scheme 1 Substrates scope of benzofuranone.^a

functional groups is good, only when electron-withdrawing groups are attached to the benzofuranones, a slight inhibitory effect on the reaction was observed. And strong electron withdrawing group would completely inhibit the reaction (**3o**). Furthermore, compared with the reactivity of HP-136 (**3d**), three benzofuranones (**3c**, **3e**, **3f**) have higher carbon radical trapping ability, which may have some potential to be used as a benzyl radical anti-oxidant.

On the other hand, the scope of toluene analogues was also tested (Scheme 2). A series of aryl-substituted toluenes were subjected to this CDC reaction to react with benzofuranone **1a**, and various products were obtained in moderate to good yields. The substituted groups with electron-donating and electron-withdrawing groups at the para or ortho position of the aryl ring could proceed smoothly to afford the desired products (**4a–4i**). In addition, the radical trapping reagent 2, 6-di-*tert*-butyl-4-methylphenol (BHT) was also applicable in this CDC reaction to furnish **4h** in 61% yield, showing that this reaction may involve a carbon radical center. These results showed that the method is suitable for multi-functionalized steric substrates. Nevertheless, for the large steric biphenyl methane, it could also get the target product **4j** in 35% yield. The reaction system could also be applied to heterocyclic systems. 6-Methylquinoline (**2k**) could also undergo CDC cross-coupling to get the product (**4k**). But 2-methylindole (**2l**) could only get the product substituted at the 3-position as a triaryl methane molecule (**4l**). Other indoles also gave the same 3-substituted indole products (**4m**, **3n**) in 76% and 55%, respectively. And the furan has two products (**4o**, **4o'**) which have been isolated respectively.⁸ It should be noted that, for the synthesis of **4p** and **4q** in Pd or Cu systems,^{7c,l} there are



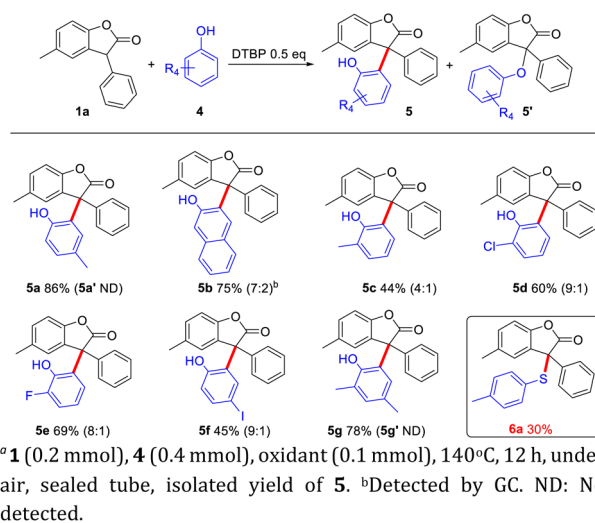


^a **1a** (0.2 mmol), oxidant (0.1 mmol), **2** (1.0 mL), 140 °C, 12 h under N₂, sealed tube, isolated yield. ^b **2k** 0.4 mmol.

Scheme 2 Substrates scope of toluene.^a

no products obtained. While this protocol can afford **4p** and **4q** in 34 and 55% yield, respectively (Scheme 2b). When we chose *n*-propyl benzene as substrate which bearing benzylic C–H bond, methylene C–H bond and methyl C–H, we can get the benzylic product **4r** in 75% yield, while only trace (<1%) amount of side-products **4r'** and **4r''** were detected (Scheme 2c). This result shows a good site-selectivity of our method.

When the steric *o*-*t*Bu substituted groups were removed from BHT, the *ortho*-C–H functionalization of phenols could engage in this process to deliver the triaryl all-carbon quaternary centers (Scheme 3). A series of phenols, such as electron-donating groups and halogen groups, were tolerated in this CDC reaction to react with benzofuranone **1a** to give **5a–5g** in good yields. Side-products of C–O construction were detected



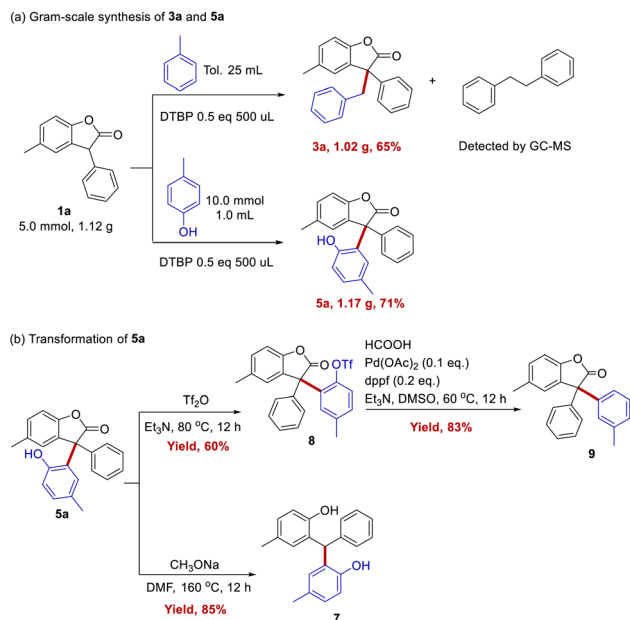
Scheme 3 Substrates scope of phenols.^a

especially in the target product (**5'**) with low yield (the ratio of **5** : **5'** is shown in the parenthesis). When there were electron donating groups in the para position of phenols, it was beneficial to the generation of radicals, so the yield would be better. When there were other groups in the ortho position of phenols, radicals were not easy to transfer, so the yield of **5** would be reduced. Halogenated phenol, especially iodophenol, were more active, and would get side reactions, leading to low yield. However, when **1a** reacted with the thiophenol, only the C–S cross coupling product was obtained (**6a**, 30%). This result was consistent with the literature,⁹ which the ortho position of phenol is indeed easy to activate as C–C bond formation rather than C–O bond formation, while that of thiophenol is more difficult to be activated, and the direct construction of C–S bond was observed.

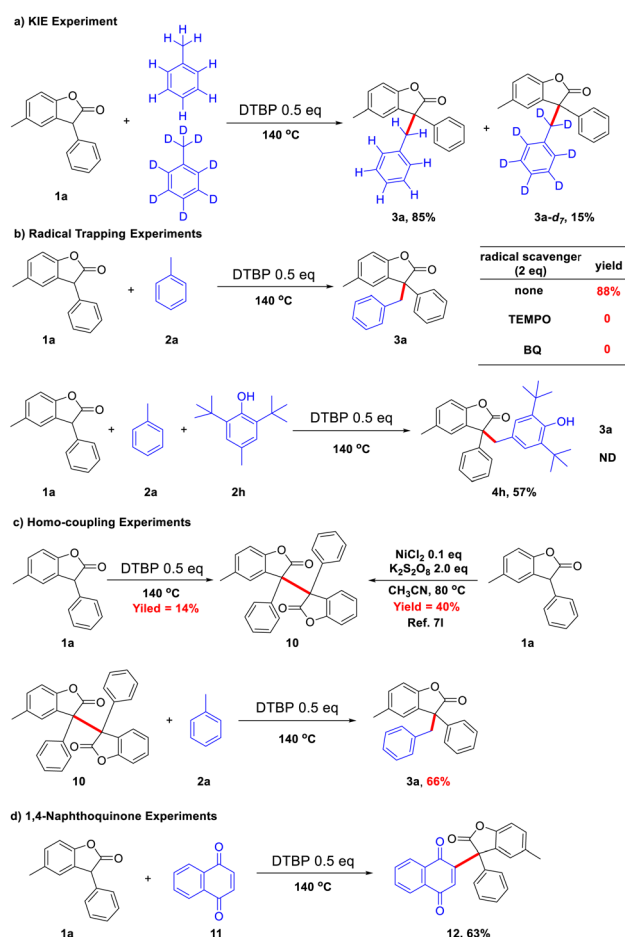
Gram scale experiments were performed for the synthesis of **3a** and **5a**, and the yields are up to 65% and 71%, respectively (Scheme 4a). Further amplify the amount of reaction may have the risk of explosion, and a special reactor would be needed. Compound **5a** contains lactone and phenol groups, making its transformation to other useful motifs possible. For example, it gave the target decarbonyl product **7** with two phenols in the yield of 85%. And it could be trifluoroacetylated by trifluoroacetic anhydride to **8** in 60% yield. Also compound **8** could undergo dehydroxylation to form product **9** with 83% yield (Scheme 4b).⁸

To probe the possible reaction mechanism, some control experiments were conducted. An intermolecular competition experiment between toluene and the deuterated toluene was carried out to investigate the kinetic isotope effect (KIE), which was found to be significant ($k_H/k_D = 5.6$) (Scheme 5a). In the hydrocarbon activation reaction, when $k_H/k_D > 2$, the cleavage of the C–H bond may be considered to be the rate-determining step of the reaction.¹⁰ The cleavage of the C–H bond may be the rate-determining step in this system. It was observed that the reaction was suppressed by the addition of a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (Tempo) and 1,4-

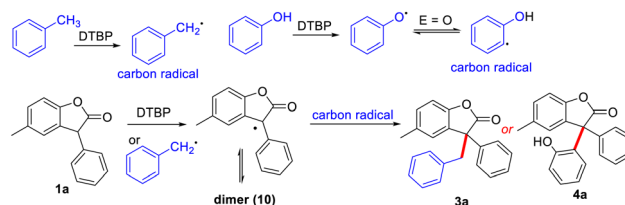




Scheme 4 Gram-scale synthesis and transformation.



Scheme 5 Control experiments.



Scheme 6 Plausible mechanism.

benzoquinone (BQ), implying the involvement of a radical species (Scheme 5b). And butylated hydroxytoluene (BHT) has trapped the radical of **1a** instead of toluene radicals. In addition, the toluene homo-coupling product was detected by GC-MS. Based on the observation, the reaction appears to go through a plausible radicals pathway. When **1a** was subjected to the reaction system without toluene, only self-coupling product **10** was obtained under the action of DTBP. And **3a** could be obtained in 66% yield from **10** after reacting with toluene (Scheme 5c). At the same time, the reaction of **1a** with naphthoquinone (**11**) did not produce naphthol, which may indicate that the reaction with phenol does not involve intermediates of quinone (Scheme 5d).

Based on the above results and those reported in the literature,^{9,11} a possible pathway for the cross-dehydrogenative coupling reaction was proposed (Scheme 6). 3-Aryl benzofuran-2(3*H*)-ones and toluene/phenols respectively generated free carbon radicals with DTBP, and then two radicals were cross-coupling to obtain **3a** and **4a**, respectively. Probably, the 3-aryl benzofuran-2(3*H*)-ones could also generate relative radical by reacting with benzyl radical species, which can be easily trapped by another benzyl radical to target products.

Conclusions

In summary, we have disclosed the first transition-metal free synthesis of all-carbon quaternary centers *via* a robust, efficient, and practical cross-dehydrogenative coupling of benzofuranones and toluenes/phenols. A diverse array of functional groups are tolerated in this transformation. A reaction mechanism with radical participation is proposed. This simple method would be useful for the synthesis of complex molecules.

Conflicts of interest

There are no conflicts to declare.

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