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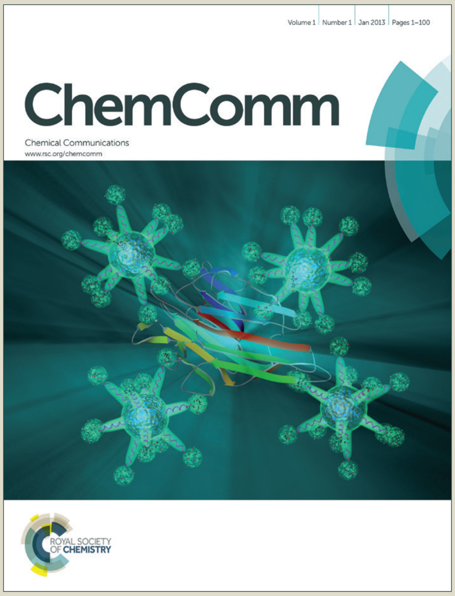

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Metal-Free Oxidative Decarbonylative Coupling of Aromatic Aldehydes with Arenes: Direct Access to Biaryls

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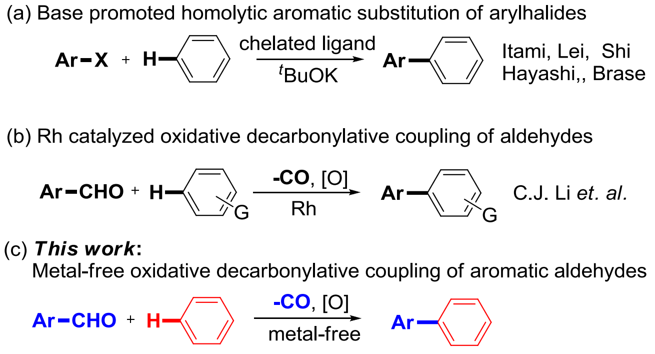
A metal-free oxidative decarbonylative coupling of aromatic aldehydes with electron-rich or electron-deficient arenes to produce biaryl compounds was developed. This novel coupling was proposed to proceed via a non-chain radical homolytic aromatic substitution (HAS) type mechanism, based on the substrates scope, *ortho*-regioselectivity, radical trapping experiments and DFT calculation studies. The ready availability of aromatic aldehydes and arenes, metal-free conditions should make this coupling attractive for the biaryl synthesis.

Biaryl scaffolds are privileged structural units that have diverse applications in the fields of pharmaceuticals, agrochemicals, functional materials and catalysts.[1] Transition metal catalyzed cross-coupling between (pseudo)aryl halides and aryl metalloids has been developed as arguably the most versatile and efficient method to synthesize such biaryl motifs, but it suffers from mainly two drawbacks: (1) it requires the pre-functionalization of both coupling partners and produces stoichiometric metal waste; (2) it requires expensive transition metal catalysts such as palladium, which would increase the difficulties and costs to remove these trace transition metal impurities from the final products after the cross-coupling at the same time.[2] Therefore, the direct biaryl synthesis from two different C-H bonds under transition-metal-free (or even metal-free) conditions is an ideal but challenging goal.[3]

For metal-free C-H arylation, homolytic aromatic substitution (HAS) of aryl radicals with benzene derivatives has been developed as a straightforward method to construct biaryl frameworks, however it has been hampered by limited precursors and laborious procedures for the generation of aryl radicals.[4] Recently, breakthroughs on base promoted homolytic aromatic substitution have been made by Itami, Lei, Hayashi, Shi and Brase, [5] where aryl radicals can be conveniently generated from aryl halides by the interaction of chelated ligands and potassium *tert*-butoxide (Scheme 1a).

On the other hand, aldehydes are cheap and readily available starting materials that have been directly used as precursors for (oxidative) decarbonylative couplings catalyzed by ruthenium or rhodium by the extensive studies of Li and co-workers since 2009 (Scheme 1b).[3b, 6] In the absence of transition metal and assisted by a suitable oxidant, aldehydes could also be converted into the corresponding acyl radicals for hydroacylation of olefins [7] and other coupling reactions [8]. These results inspire us to conceive the generation of aryl radicals from aromatic aldehydes by the further decarbonylation of these acyl radials under oxidative conditions.[7b, 9] *Herein, we report the first metal free oxidative decarbonylative coupling of aromatic aldehydes with electron-rich or electron-deficient arenes to produce biaryl compounds through a radical pathway* (Scheme 1c).



Scheme 1 Direct arene C-H transformations for biaryl synthesis.

We first examined the oxidative decarbonylative coupling of *p*-methoxycarbonyl benzaldehyde (**1a**)[10] in benzene with TBP (di-*tert*-butyl peroxide) as the initiator and oxidant. The desired biaryl product **3a** was detected by GC-MS, but in very low yield (< 2 %), and the most of the aldehyde **1a** remained intact. During the subsequent optimization, by ordinary solvent screening, we surprisingly found that the nitrobenzene was able to increase the yield noticeably, and the addition of 2 equiv of nitrobenzene afforded biaryl product **3a** in 22 % yield (Table 1, entry 2). At the beginning, the role of nitrobenzene as the additive to this reaction was unclear so other nitro-containing compounds such as *p*-nitrobenzoic acid and *p*-nitrobenzoyl chloride were tried, which indeed afford better yields than nitrobenzene itself (entries 3 and 4).

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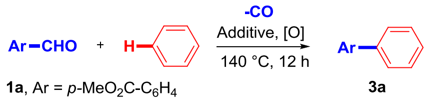
It seems that nitro containing electron-deficient arenes can improve this coupling so the three regioisomers of dinitrobenzene (*o*, *m* and *p*) were tested next (entries 6-8) and *o*-dinitrobenzene (abbreviated as DNB next) afforded the best yield (60 %, entry 8). The further fine adjustment of dosage of DNB (entries 7-9) and reaction temperature (entry 10) led to an optimal yield of 68 %. It is noteworthy that the *tert*-butylhydroperoxide (TBHP) can also be used as the initiator and oxidant to give similar results; but dioxygen was ineffective (entries 11 and 12). When a mixed-solvent of benzene/dichloroethane (DCE) or benzene/acetonitrile was applied instead of benzene alone, the yields of desired biaryl product **3a** dropped to 43 % and 35 %, respectively (entries 14 and 15). Transition-metals such as copper and iron that have been widely used as redox catalysts for aldehydes C(sp^2)-H transformations[11] were ineffective for this oxidative decarbonylative coupling (see Supporting Information).

Table 1 Optimization of the metal-free oxidative decarbonylative coupling [a]



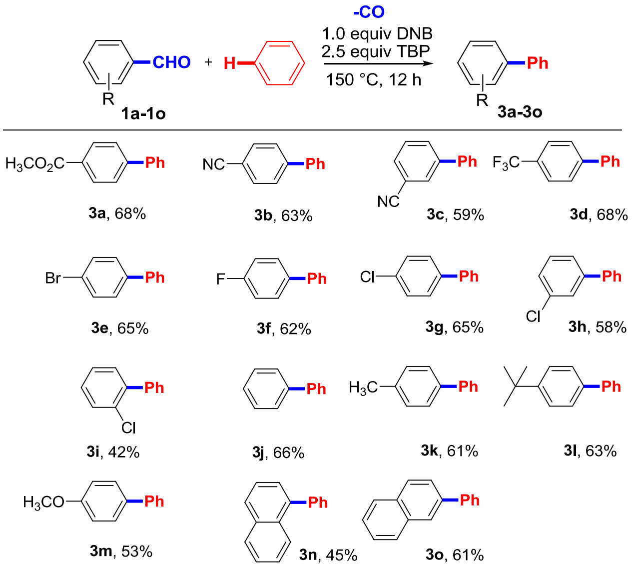
entry	Additive (equiv)	[O] (equiv)	yield [%] [b]
1	--	TBP (2.5)	< 2%
2	NO$_2$-C$_6$H$_5$ (2.0)	TBP (2.5)	22
3	*p*-NO$_2$-C$_6$H$_4$CO$_2$H (2.0)	TBP (2.5)	38
4	*p*-NO$_2$-C$_6$H$_4$COCl (2.0)	TBP (2.5)	54
5	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (2.0)	TBP (2.5)	60
6	1,3-(NO$_2$)$_2$-C$_6$H$_4$ (2.0)	TBP (2.5)	56
7	1,4-(NO$_2$)$_2$-C$_6$H$_4$ (2.0)	TBP (2.5)	48
8	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (1.0)	TBP (2.5)	64
9	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (0.5)	TBP (2.5)	46
10 [c]	**1,2-(NO$_2$)$_2$-C$_6$H$_4$ (1.0)**	**TBP (2.5)**	**68**
11	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (2.0)	TBHP (2.5)	63
12	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (2.0)	O$_2$	< 2%
13	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (2.0)	TBP (2.0)	57
14 [d]	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (2.0),	TBP (2.5)	43
15 [e]	1,2-(NO$_2$)$_2$-C$_6$H$_4$ (2.0),	TBP (2.5)	35

[a] Conditions: **1a** (0.2 mmol), additive, TBP (2.5 equiv, 0.5 mmol), benzene (80 equiv, 16.0 mmol, 1.5 mL), reacted for 12 h at 140°C under argon atmosphere unless otherwise noted. [b] Isolated yields. [c] Reacted at 150°C. [d] Mixed-solvent of benzene/DCE (0.75 mL/0.75 mL). [e] Mixed-solvent of benzene/ acetonitrile (0.75 mL/0.75 mL).

Under the optimized conditions (Table 1, entry 10), the substrate scope and limitation of this oxidative decarbonylative coupling of aldehydes with arenes were explored. The effect of substituents on the aromatic aldehyde moiety is listed in Table 2. Benzaldehydes bearing electron withdrawing or donating substituents were successfully transformed into the desired decarbonylated biaryl products in moderate yields, such as cyano (**1b** and **1c**), trifluoromethyl (**1d**), halo (**1e-1i**), alkyl (**1k** and **1l**) and methoxyl group (**1m**). Besides substituted benzaldehydes, the optimized reaction conditions can also be applied to the coupling of . or -naphthaldehyde (**1n** and **1o**) with benzene. Unfortunately, this oxidative decarbonylative coupling failed for the aliphatic aldehydes such as *n*-butanal and cyclohexane carbaldehyde; no corresponding alkylated products was detected by the GC-MS and the aliphatic carboxylic acids were revealed as the main product.[12]

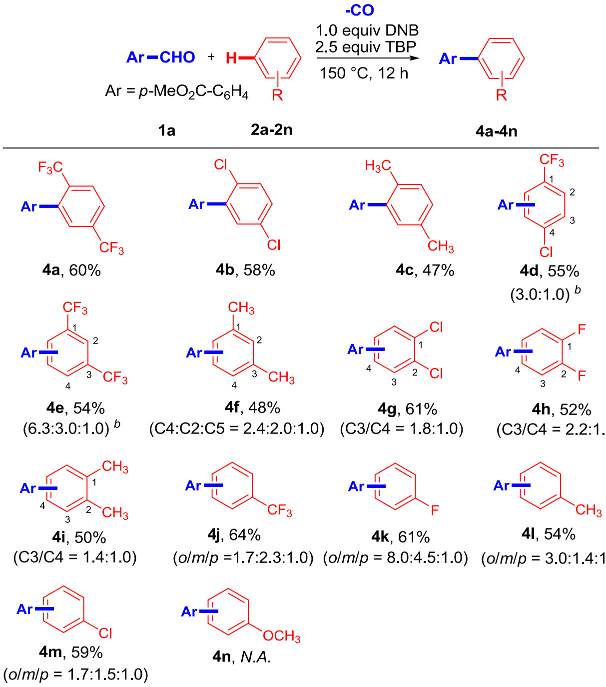
On the other hand, for different arene (C-H) coupling partners (Table 3), the optimized reaction condition was applicable to both electron-deficient arenes such as **2a** and slightly electron-rich arenes such as **2c**, but not suitable for more electron-rich anisole (**2n**). For the arenes (**2d-2m**) that was capable of generating regioisomers, the oxidative decarbonylative coupling subjected to afford the *ortho*-functionalized products predominately. It is worth noting that the biaryl methanone byproduct (that could be generated from the acyl radical without decarbonylation) was not detected by the GC-MS and crude ^{1}H NMR for all of the substrates tested, which might imply that the decarbonylation is a rapid step in this reaction.

Table 2 The influence of aromatic aldehydes on the metal-free oxidative decarbonylative coupling



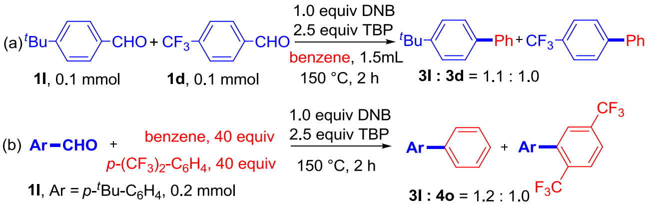
Conditions: **1a-1o** (0.2 mmol), DNB (1 equiv, 0.2 mmol), TBP (2.5 equiv, 0.5 mmol), benzene (80 equiv, 16.0 mmol, 1.5 mL), reacted for 12 h at 150°C under argon atmosphere unless otherwise noted. Isolated yields were reported.

Table 3 The influence of arenes on the metal-free oxidative decarbonylative coupling [a]



[a] Conditions: **1a** (0.2 mmol), arene (**2a-2n**) (1.5 mL), DNB (1 equiv, 0.2 mmol), TBP (2.5 equiv, 0.5 mmol), reacted for 12 h at 150°C under argon atmosphere unless otherwise noted. Isolated yields were reported. The ratio of isomers was determined by ^{1}H NMR and assigned by comparing with the data reported by literatures. [b] The ratio was not assigned.

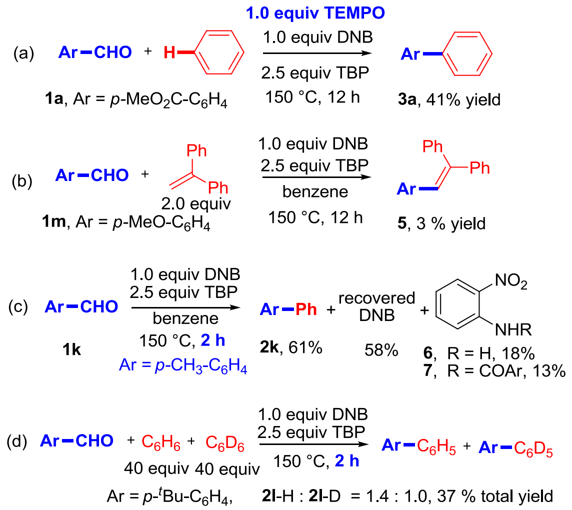
The oxidative decarbonylative coupling fitted well with electron-deficient arenes, which differentiates it from the Friedel-Crafts type reactions and transition-metal catalyzed aromatic C-H activation via electrophilic substitution mechanism. In the preliminary competition reactions, the aldehydes and arenes with different electron densities showed comparable reaction rate (Scheme 2, see Supporting Information for details). Considering that peroxide is reported as a good radical initiator for aldehydes [7, 8b, 13] and the obvious *ortho*-selectivity demonstrated by arene coupling partners (Table 2), we speculated this reaction proceeded through the homolytic aromatic substitution (HAS) type pathway.



Scheme 2 Competition reactions of the oxidative decarbonylative coupling.

Next, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, 1.0 equiv) as radical inhibitor was subjected to the standard procedure, which still led to 41 % yield of product **3a** (Scheme 3a), and thus a chain radical mechanism might be unlikely. When 1,1-diphenylethene (2.0 equiv) as radical scavenger was added in, the corresponding aryl radical was trapped to afford triarylethene **5** in low yield (3 %, Scheme 3b),[14] which further strongly supports the generation of aryl radical during the reaction.

DNB played a critical role in this oxidative decarbonylative coupling. By carefully balancing the DNB during the reaction, 58 % was recovered after the coupling and small part of it was reduced and converted to 2-nitroaniline (**6**) and N-acyl-2-nitroaniline (**7**) in 18 % and 13 % yield, respectively (Scheme 3c). The reduction of the nitro group might arise from a single electron transfer to DNB.[15] Since DNB and its two regioisomers (*meta* and *para*) were famous for their electron-deficient character and thus used as electron acceptors on the study of radical nucleophilic substitution mechanism between a carbon anion with halobezenes,[16] we speculated that DNB acted as an electron acceptor here too, although other possible pathways could not be ruled out at this stage.



Scheme 3 Mechanistic investigation on the metal-free oxidative decarbonylative coupling.

With the reaction of benzaldehyde (**1j**) and chlorobenzene (**3m**) as an example, a plausible mechanism was proposed in Figure 1, which was assisted by the DFT calculation (B3LYP/6-31+G (d) method, see Supporting Information). First, the *tert*-butoxy radical abstracts the aldehyde hydrogen atom to provide the acyl radical **I**, which undergoes decarbonylation to afford phenyl radical **II**. Addition of the phenyl radical to chlorobenzene gives the phenylcyclohexadienyl radical **III**. Due to the "persistent radical effect",[17] the direct tertiary hydrogen abstraction of radical **III** by *tert*-butoxy radical to realize re-aromatization is dynamically unbeneficial. Instead, radical **III** transfers an electron to DNB to produce phenylcyclohexadienyl cation **IV** and DNB$^{\bullet-}$, which is further deprotonated by *tert*-butoxide anion to afford the biaryl product (a cation/anion complex is formed before the deprotonation implied by the IRC analysis of Gaussian). DNB$^{\bullet-}$ can be recovered by transferring the superfluous electron to TBP to accelerate its heterolytic cleavage, or transferring the electron to *tert*-butoxy radical to produce *tert*-butoxide anion. As a side reaction, DNB$^{\bullet-}$ can also be reduced to yield 2-nitroaniline **6** (Scheme 3c) and N-acyl-2-nitroaniline[18] byproducts **7**.

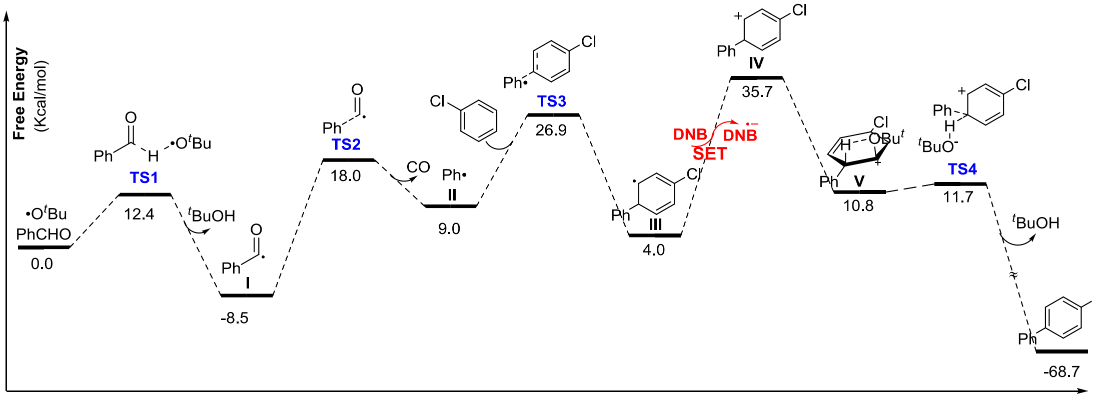


Figure 1. Free energy profiles for the proposed mechanism of this oxidative decarbonylative coupling. Calculated at the B3LYP/6-31+G (d) basis with IEF-PCM solvation corrections for chlorobenzene at 298K.

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The phenylcyclohexadienyl cation **IV** is 35.7 Kcal/mol higher in free energy than the radical **III**. The activation energies for SET are often close to the reaction free energies using Marcus theory,[19] and thus the activation barrier of SET is roughly estimated as $\Delta G^{act}{}_{SET} \approx$ 35.7 Kcal/mol. By comparing $\Delta G^{act}{}_{SET}$ with the activation energies of transition states (**TS1**-**TS4**) obtained by DFT calculation, the rate-determine step might be the SET step. The low KIE value (1.41) obtained from the competition reaction between C_6H_6 and C_6D_6 with aldehyde **1l** further confirmed the deprotonation was not the rate-determine step (Scheme 3d).

In conclusion, we have developed the first metal-free oxidative decarbonylative coupling of aromatic aldehydes with electron-rich or electron-deficient arenes to produce biaryl compounds. The substrate scope, *ortho*-regioselectivity, radical trapping experiments and DFT calculations supported a non-chain radical homolytic aromatic substitution (HAS) type mechanism and DNB acted as the electron "porter". The ready availability of aromatic aldehydes and arenes, metal-free conditions should make this oxidative decarbonylative coupling attractive for the biaryl synthesis. The further improvement and detailed mechanism are ongoing in our laboratory.

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The authors declare no competing financial interest.

Notes and references

1 For recent reviews on applications of biaryl units, see: (a) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, **2002**, *102*, 1359; (b) M. C. Kozlowski, B. J. Morgan and E. C. Linton, *Chem. Soc. Rev.*, **2009**, *38*, 3193; (c) D. S. Surry and S. L. Buchwald, *Angew. Chem. Int. Ed.*, **2008**, *47*, 6338; (d) R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, **2008**, *41*, 1461.

2 For selected examples on Metal-Catalyzed Cross-Coupling Reactions, see: (a) *Metal-Catalyzed Cross-Coupling Reactions and More*, Eds.: A. de Meijere, S. Bräse and M. Oestreich, Wiley-VCH, Weinheim, **2014**; (b) C. C. C. J. Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, *Angew. Chem. Int. Ed*., **2012**, *51*, 5062; (c) J.-P. Corbet and G. Mignani, *Chem. Rev*., **2006**, *106*, 2651; d) M. Catellani, E. Motti, N. Della Ca and R. Ferraccioli, *Eur. J. Org. Chem*., **2007**, 4153.

3 Direct C-H arylations has developed as an efficient complement, see: (a) I. Hussaina and T. Singh, *Adv. Synth. Catal.*, **2014**, *356*, 1661; (b) A. Dermenci and G. Dong, *Sci. China Chem*., **2013**, *56*, 685; (c) D.-G. Yu, B.-J. Li and Z.-J. Shi, *Tetrahedron*, **2012**, *68*, 5130; (d) J. A. Ashenhurst, *Chem. Soc. Rev.*, **2010**, *39*, 540; (e) C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.*, **2011**, *111*, 1780. (f) C. S. Yeung and V. M. Dong, *Chem. Rev.*, **2011**, *111*, 1215.

4 For reviews on HAS, see: (a) W. R. Bowman and J. M. D. Storey, *Chem. Soc. Rev.*, **2007**, *36*, 1803; (b) R. Bolton and G. H. Williams, *Chem. Soc. Rev.*, **1986**, *15*, 261; (c) A. Studer and M. Bossart, In *Radicals in Organic Synthesis*; Eds.: P. Renaud, M. P. Sibi, Wiley-VCH; Weinheim, **2001**; Vol. *2*, Chapter 1.4, pp 62-80.

5 (a) S. Yanagisawa, K. Ueda, T. Taniguchi and K. Itami, *Org. Lett.* **2008**, *10*, 4673; (b) S. Yanagisawa and K. Itami, *ChemCatChem*, **2011**, *3*, 827; (c) W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong and A. Lei, *J. Am. Chem. Soc*., **2010**, *132*, 16737; (d) E. Shirakawa, K.-i. Itoh, T. Higashino and T. Hayashi, *J. Am. Chem. Soc.*, **2010**, *132*, 15537; (e) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li and Z.-J. Shi, *Nat. Chem*., **2010**, *2*, 1044; (f) K.-S. Masters and S. Brase, *Angew. Chem. Int. Ed*., **2013**, *52*, 866; (g) A. Studer and S. Amrein, *Angew. Chem. Int. Ed*., **2000**, *39*, 3080; (h) A. Studer and D. P. Curran, *Angew. Chem. Int. Ed*., **2011**, *50*, 5018.

6 (a) X. Guo, J. Wang and C. J. Li, *J. Am. Chem. Soc*., **2009**, *131*, 15092; (b) Q. Shuai, L. Yang, X. Guo, O. Basle and C. J. Li, *J. Am. Chem. Soc.*, **2010**, *132*, 12212; (c) X. Guo, J. Wang and C.J. Li, *Org. Lett*., **2010**, *12*, 3176; (d) L. Yang, C. A. Correia, X. Guo and C. J. Li, *Tetrahedron Lett*., **2010**, *51*, 5486; (e) L. Yang, X. Guo and C.J. Li, *Adv. Synth. Catal*., **2010**, *352*, 2899; (f) L. Yang, T. Zeng, Q. Shuai, X. Guo and C.J. Li, *Chem. Comm*., **2011**, *47*, 2161.

7 For radial-type hydroacylation of olefins, see: (a) C. Chatgilialoglu, D. Crich, M. Komatsu and I. Ryu, *Chem. Rev*., **1999**, *99*, 1991; (b) V. Chudasama, R. J. Fitzmaurice and S. Caddick, *Nat. Chem*., **2010**, *2*, 592; (c) V. Chudasama, R. J. Fitzmaurice, J. M. Ahern and S. Caddick, *Chem. Comm*., **2010**, *46*, 133; (d) R. J. Fitzmaurice, J. M. Ahern and S. Caddick, *Org. Biolmol. Chem*., **2009**, *7*, 235; (e) S. Esposti, D. Dondi and M. Fagnoni, A. Albini, *Angew. Chem. Int. Ed*., **2007**, *46*, 2531; (f) S. Tsujimoto, T. Iwahama, S. Sakaguchi and Y. Ishii, *Chem. Commun.*, **2001**, 2352; (g) S. Tsujimoto, S. Sakaguchi and Y. Ishii, *Tetrahedron Lett*., **2003**, *44*, 5601.

8 (a) K. Matcha and A. P. Antonchick, *Angew. Chem. Int. Ed*., **2013**, *52*, 2082; (b) M.-B. Zhou, R.-J. Song, X.-H. Ouyang, Y. Liu, W.-T. Wei, G.-B. Deng and J.-H. Li, *Chem. Sci.*, **2013**, *4*, 2690.

9 (a) E. Watanabe, A. Kaiho, H. Kusama and N. Iwasawa, *J. Am. Chem. Soc*., **2013**, *135*, 11744; (b) Y.-J. Jang, M.-C. Yan, Y.-F. Lin and C.-F. Yao, *J. Org. Chem.*, **2004**, *69*, 3961.

10 The ester group would make the biaryl product not so volatile.

11 For selected examples of aldehyde C(sp^2)-H transformations promoted by oxidant/transition-metal combination, see: (a) J. Wang, C. Liu, J. Yuan and A. Lei, *Chem. Commun*., **2014**, *50*, 4736; (b) J. Wang, C. Liu, J. Yuan and A. Lei, *Angew. Chem. Int. Ed*., **2013**, *52*, 2256; (c) B.-X. Tang, R.-J. Song, C.-Y. Wu, Y. Liu, M.-B. Zhou, W.-T. Wei, G.-B. Deng, D.-L. Yin and J.-H. Li, *J. Am. Chem. Soc*., **2010**, *132*, 8900.

12 For *n*-butanal, the self-aldol condation by-product was also detected. A control reaction using benzoic acid as the starting material to replace benzaldehyde failed to afford the biphenyl product, which could exclude the oxidation-decarboxylation-coupling pathway.

13 (a) J. Liu, C. Shao, Y. Zhang, G. Shi and S. Pan, *Org. Biomol. Chem*., **2014**, *12*, 2637; (b) C. Li, L. Wang, P. Li and W. Zhou, *Chem. Eur. J.*, **2011**, *17*, 10208; (c) O. Basle, J. Bidange, Q. Shuai and C.-J. Li, *Adv. Synth. Catal.*, **2010**, *352*, 1145. (d) F. Xiao, Q. Shuai, F. Zhao, O. Basle, G.-J. Deng and C.-J. Li, *Org. Lett*., **2011**, *13*, 1614.

14 The trapping of aryl radical by 1,1-diphenylethene was reported by: C.-L. Sun, Y.-F. Gu, B. Wang and Z.-J. Shi, *Chem. Eur. J.*, **2011**, *17*, 10844.

15 (a) Y. Mori, *J. Phys. Org. Chem*., **2014**, *27*, 803; (b) X.-M. Zhang, D.-L. Yang and Y.-C. Liu, *J. Org. Chem.*, **1993**, 58, 224; (c) S. F. Nelsen, M. N. Weaver, A. E. Konradsson, J. P. Telo and T. Clark, *J. Am. Chem. Soc*., **2004**, *126*, 15431.

16 (a) N. Zhang, S. R. Samanta, B. M. Rosen and V. Percec, *Chem. Rev*., **2014**, *114*, 5848; (b) R. A. Rossi, A. B. Pierini and A. B. Penenory, *Chem. Rev*., **2003**, *103*, 71.

17 H. Fischer, *Chem. Rev.*, **2001**, *101*, 3581.

18 The acylation of amines by aldehydes in the presence of peroxides have previously been reported: (a) F. Xiao, Y. Liu, C. Tang and G.-J. Deng, *Org. Lett*., **2012**, *14*, 984; (b) G. S. Kumar, R. A. Kumar, P. S. Kumar, N. V. Reddy, K. V. Kumar, M. L. Kantam, S. Prabhakar and K. R. Reddy, *Chem. Commun.*, **2013**, *49*, 6686; (c) X. Guo, L. Tang, Y. Yang, Z. Zha and Z. Wang, *Green Chem*., **2014**, *16*, 2443.

19 (a) C. Dey, E. Larionov and E. P. Kundig, *Org. Biomol. Chem.***, 2013**, *11*, 6734; (b) G. O. Jones, P. Liu, K. N. Houk and S. L. Buchwald, *J. Am. Chem. Soc*., **2010**, *132*, 6205.