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Metal-free cross-dehydrogenative coupling of aryl aldehydes to give symmetrical carboxylic anhydrides promoted by the TBHP/*n*Bu₄PBr system

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Abstract- A novel, efficient and metal-free dual C–O bond formation reaction for the synthesis of carboxylic anhydrides from aryl aldehydes *via* cross-dehydrogenative coupling is described. Heating a mixture of aromatic aldehydes and an aqueous solution of *tert*-butyl hydroperoxide as oxidant in the presence of catalytic *n*Bu₄PBr in chlorobenzene at 80 °C for 3 h afforded the corresponding carboxylic anhydrides in good to excellent yields.

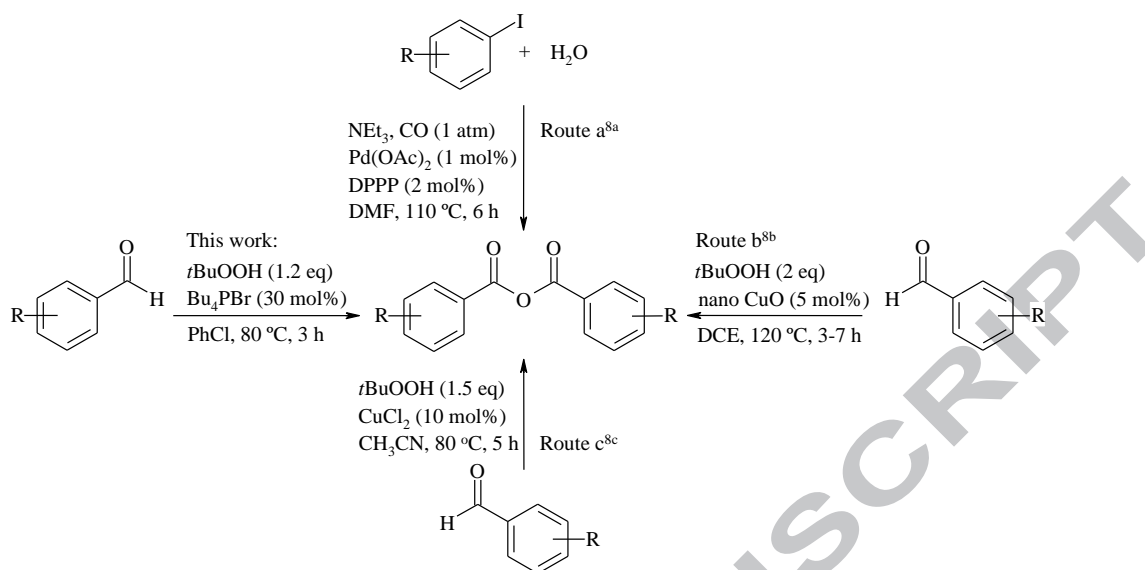
Keywords: cross-dehydrogenative coupling, metal-free conditions, dual C–O bond formation, *n*Bu₄PBr, *tert*-butyl hydroperoxide, carboxylic anhydrides, aldehydes

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The transition-metal-free C–H functionalization of organic substrates is a versatile and powerful tool in current organic chemistry. An overwhelming amount of current C–H activation methods use transition metals while the area of transition metal free C–H activation remains relatively unexplored.¹ Furthermore, the development of C–H oxygenation of organic molecules using oxidants such as *tert*-butyl hydroperoxide (TBHP), Oxone, O₂, phthaloyl peroxide (PPO) is a significant challenge and remains highly desirable,² because the use of oxidants in the presence or absence of transition-metals has gained a great deal of attention for the preparation of complex compounds in synthetic organic chemistry. Amazing and unpredictable chemistry of these compounds, has led to the researchers interest in the use of oxidants in their reactions. On the other hand, functionalization of C–H bonds through cross-dehydrogenative coupling (CDC) reactions has played a crucial role for the preparation of a wide variety of organic compounds.³ Very recently, the application of TBHP as a powerful oxidant in combination with Bu₄NX catalysts has received attention for the formation of C–C, C–N, C–O and C–S bonds.⁴

Carboxylic anhydrides are of great significance for the preparation of a variety of carboxylic acid derivatives such as amides and esters⁵ as well as drug and peptide synthesis.⁶

Up to now, a great deal of attention has been focused on finding new approaches for the preparation of carboxylic anhydride derivatives.⁷ Xiao and co-workers have reported a remarkable synthesis of carboxylic anhydrides *via* the Pd-catalyzed carbonylation of aryl halides at atmospheric CO pressure^{8a} (Scheme 1, route a). Recently, Patel and co-workers reported a nano-CuO catalyzed CDC reaction for the synthesis of symmetrical anhydrides from aldehydes using TBHP as an oxidant^{8b} (Scheme 1, route b). Very recently, Saberi and co-workers developed the oxidative self-coupling of aldehydes in the presence of a CuCl₂/TBHP system^{8c} (Scheme 1, route c). As part of our continuing effort to develop efficient methods for the preparation of organic compounds from readily available starting materials,⁹ herein, we report the preparation of symmetrical carboxylic anhydrides from inexpensive and readily available aldehydes, promoted by a TBHP/Bu₄PBr system without the aid of a transition-metal catalyst (Scheme 1).



Scheme 1. Some recent synthetic strategies for carboxylic anhydrides

To begin our study, we optimized the reaction conditions for the formation of benzoic anhydride **2a** from benzaldehyde **1a** as a model substrate (Table 1). The effect of various oxidants, reaction solvents, additives and reaction temperature were examined. At first, the reaction was carried out in the presence of TBHP (1 eq.) as oxidant and TBPB (15 mol%) as additive in chlorobenzene at ambient temperature. These reaction conditions proved to be ineffective (Table 1, entry 1) however, when the temperature was raised to 50 °C and 80 °C, the desired product **2a** was obtained in 20% and 55% yields, respectively (entries 2,3). By increasing amount of TBHP to 1.2 eq., the yield improved to 70% (entry 4). When the reaction was performed with 30 mol% of TBPB, a maximum yield of 85% was observed (entry 5). We also tested a higher reaction temperature of 100 °C and an increased amount of TBHP (1.5 eq.), however the yield of **2a** decreased to 72% and 78% respectively (entries 6 and 7). Furthermore, increasing the reaction time to 6 h led to a lower yield (entry 8). When the quantity of TBPB increased to 40 mol%, the yield of the product did not improve (entry 9). Next, the effects of other additives such as TBAB, Aliquat 336, KI, I₂ and CuI was examined but the results were not acceptable (entries 10–14). Other oxidants were also tested. Benzoyl peroxide (BPO) gave **2a** in 65% yield (entry 15) while K₂S₂O₈ as well as (NH₄)₂S₂O₈ were ineffective (entries 16, 17). Upon the screening of solvents, we found that PhCl was the most suitable. Carrying out the reaction in CH₃CN, DCE, PhCH₃ and 1,4-dioxane resulted in decreased yields (entries 18–20, 23). In DMSO, H₂O and DMSO/H₂O the reaction did not proceed (entries 21, 22, 24).

Finally, in the absence of TBHP (entry 25) and TBPB (entry 26), formation of **2a** was not detected, which indicated that both TBHP and TBPB were crucial to the reaction. Thus, the optimal conditions for the conversion of benzaldehyde **1a** to benzoic anhydride **2a** were determined: TBHP (1.2 eq.) and TBPB (30 mol%), in chlorobenzene at 80 °C for 3 h (Table 1, entry 5).¹⁰

Table 1. Condition screening for the CDC formation of benzoic anhydride **2a** from benzaldehyde **1a**^a

$2 \times \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \xrightarrow[\text{solvent}]{\text{Oxidant, additive}} \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$

1a **2a**

Entry	Oxidant (eq.) ^b	Additive (mol%) ^b	Solvent	Temp (°C)	Yield (%) ^c
1	TBHP ^d (1)	TBPB ^e (15)	PhCl	25	NR ^f
2	TBHP (1)	TBPB (15)	PhCl	50	20
3	TBHP (1)	TBPB (15)	PhCl	80	55
4	TBHP (1.2)	TBPB (15)	PhCl	80	70
5	TBHP (1.2)	TBPB (30)	PhCl	80	85
6	TBHP (1.2)	TBPB (30)	PhCl	100	72
7	TBHP (1.5)	TBPB (30)	PhCl	80	78
8 ^g	TBHP (1.2)	TBPB (30)	PhCl	80	65
9	TBHP (1.2)	TBPB (40)	PhCl	80	85
10	TBHP (1.2)	TBAB (30)	PhCl	80	70
11	TBHP (1.2)	Aliquat 336 ^h (30)	PhCl	80	35
12	TBHP (1.2)	KI (30)	PhCl	80	trace
13	TBHP (1.2)	I ₂ (30)	PhCl	80	NR
14	TBHP (1.2)	CuI (30)	PhCl	80	NR
15	BPO ⁱ (1.2)	TBPB (30)	PhCl	80	65
16	K ₂ S ₂ O ₈ (1.2)	TBPB (30)	PhCl	80	NR
17	(NH ₄) ₂ S ₂ O ₈ (1.2)	TBPB (30)	PhCl	80	NR
18	TBHP (1.2)	TBPB (30)	CH ₃ CN	80	55
19	TBHP (1.2)	TBPB (30)	DCE	80	50
20	TBHP (1.2)	TBPB (30)	PhCH ₃	80	50
21	TBHP (1.2)	TBPB (30)	DMSO	80	NR
22	TBHP (1.2)	TBPB (30)	H ₂ O	80	NR
23	TBHP (1.2)	TBPB (30)	1,4-Dioxane	80	trace
24	TBHP (1.2)	TBPB (30)	DMSO:H ₂ O (1:1)	80	NR
25	–	TBPB (30)	PhCl	80	NR
26	TBHP (1.2)	–	PhCl	80	NR

^aReaction conditions: **1a** (0.5 mmol), solvent (0.75 mL), 3 h; ^bWith respect to **1a**; ^cIsolated yields; ^d*t*-BuOOH in H₂O (70 wt%); ^eTetrabutylphosphonium bromide; ^fNR = no reaction; ^gReaction time of 6 h; ^hTricaprylmethylammonium chloride; ⁱBenzoyl peroxide.

After optimization of the reaction conditions, a series of aromatic anhydrides **2a–t** were prepared from various aromatic aldehydes **1a–t** (Table 2). Electron-donating substituents, such as CH₃ and methoxy, regardless of their positions on the aryl ring, gave the corresponding anhydrides **2b–j** in 60–86 % yields (entries 2–10). Aromatic aldehydes with electron-withdrawing substituents such as NO₂ and halogen groups

were ineffective in this reaction and the corresponding anhydrides **2k–o** were not detected in the reaction mixtures (entries 11–15). Naphthalene carbaldehydes (**1p** and **1q**) were also suitable for this CDC reaction and afforded 1-naphthoic- and 2-naphthoic anhydrides **2p** and **2q** in 70%, 72% yields, respectively (entries 16,17). Cinnamaldehyde was also subjected to the reaction which gave anhydride **2r** in 51% yield (entry 18). Furthermore, heteroaromatic aldehydes such as furan-2-carbaldehyde and thiophene-2-carbaldehyde were also examined affording anhydrides **2s** and **2t** in 76% and 82% yields, respectively (entries 19 and 20).¹⁰

Table 2. Substrate scope for the synthesis of carboxylic anhydrides **2a–t**^a

$2 \times \text{Ar}-\text{CHO} \xrightarrow[\text{TBPB, PhCl, 80 } ^\circ\text{C, 3 h}]{t\text{BuOOH (1.2 eq)}} \text{Ar}-\text{CO}-\text{O}-\text{CO}-\text{Ar}$

$\text{1a-t} \qquad \qquad \qquad \text{2a-t}$

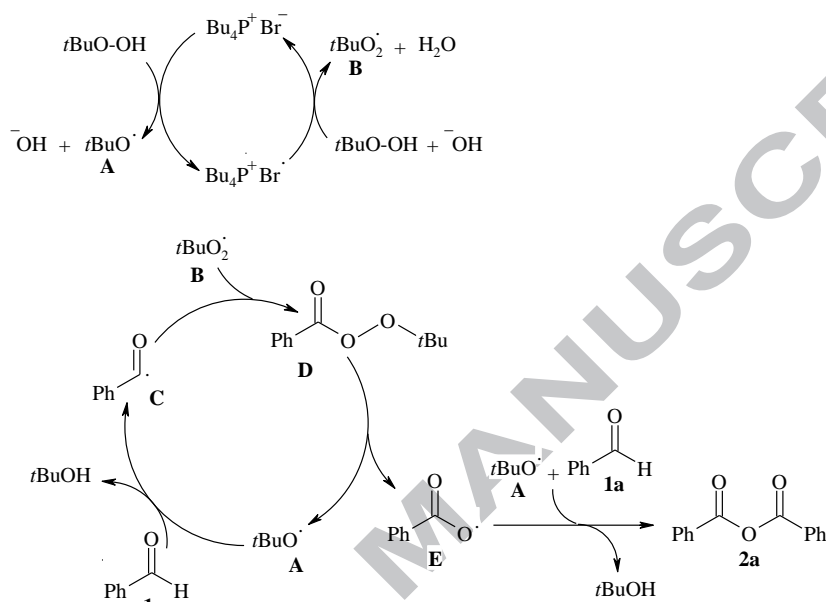
Entry	1	Ar	2	Yield (%) ^b
1	1a	Ph	2a	85
2	1b	2-CH ₃ C ₆ H ₄	2b	78
3	1c	3-CH ₃ C ₆ H ₄	2c	80
4	1d	4-CH ₃ C ₆ H ₄	2d	78
5	1e	2,5-(CH ₃) ₂ C ₆ H ₃	2e	86
6	1f	2-CH ₃ OC ₆ H ₄	2f	73
7	1g	3-CH ₃ OC ₆ H ₄	2g	76
8	1h	4-CH ₃ OC ₆ H ₄	2h	70
9	1i	2,5-(CH ₃ O) ₂ C ₆ H ₃	2i	60
10	1j	3,4-(CH ₃ O) ₂ C ₆ H ₃	2j	63
11	1k	2-ClC ₆ H ₄	2k	NR
12	1l	4-ClC ₆ H ₄	2l	NR
13	1m	4-FC ₆ H ₄	2m	NR
14	1n	4-BrC ₆ H ₄	2n	NR
15	1o	4-O ₂ NC ₆ H ₄	2o	NR
16	1p	1-Naphthyl	2p	70
17	1q	2-Naphthyl	2q	72
18	1r	<i>trans</i> -PhCH=CH-	2r	51
19	1s	2-Furyl	2s	76
20	1t	2-Thienyl	2t	82

^aReaction conditions: aryl aldehyde (**1**, 0.5 mmol), TBHP (0.6 mmol), TBPB (30 mol%), PhCl (0.75 mL), 80 °C, 3 h.

^bIsolated yields.

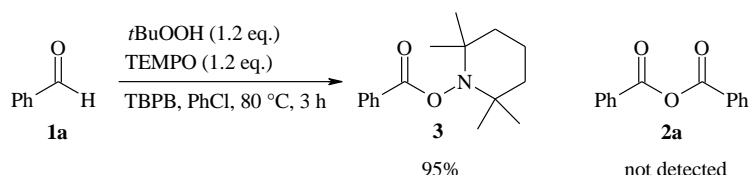
A reasonable mechanism for the formation of benzoic anhydride **2a** is provided in Scheme 2. Initially, TBPB reacts with TBHP to give *tert*-butoxy **A** and *tert*-butylperoxy **B** radicals.^{4b,8b,11} Next, the *tert*-butoxy radical **A** removes a hydrogen atom from benzaldehyde **1a** to form benzoyl radical **C**, which can be trapped by *tert*-

butylperoxy radical **B** through a C–O bond formation to give *tert*-butyl peroxybenzoate^{8b,11g} **D**. The latter may undergo O–O bond cleavage to release benzoyloxy radical **E** and return *tert*-butoxy radical **A** to the reaction cycle. Finally, benzoyloxy radical **E** and benzoyl radical **C** are coupled through a C–O bond formation to afford benzoic anhydride **2a**.



Scheme 2. Proposed reaction mechanism for the cross-dehydrogenative self-coupling of benzaldehyde **1a** and formation of benzoic anhydride **2a** promoted by $n\text{Bu}_4\text{PBr/TBHP}$ system

To provide evidence for the proposed radical mechanism of the CDC reaction, the reaction of benzaldehyde **1a** under the optimized reaction conditions was carried out in the presence of the radical trap TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl. In this reaction, 2,2,6,6-tetramethylpiperidino benzoate **3** was isolated in 95% yield and the desired anhydride **2a** was not detected (Scheme 3). This observation strengthens presence of a radical intermediate in the examined CDC reaction.



Scheme 3. Trapping of benzoyl radical with TEMPO

In conclusion, we have disclosed a practical, and metal-free oxidative cross-dehydrogenative self-coupling of aldehydes. This CDC coupling for the preparation of carboxylic anhydrides through dual C–O bond formation was promoted by a *n*Bu₄PBr/TBHP system using TBHP for oxygen atom transfer. This novel, efficient and economical approach was carried out using the inexpensive TBHP/TBPB system, under mild and neutral reaction conditions, with moderate temperatures, short times and without the aid of a transition metal. To the best of our knowledge this is the first report on the use of tetraalkylphosphonium halides as a catalyst in CDC reactions.

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References and notes:

1. (a) Sun, C. L.; Shi, Z. J. *Chem. Rev.* **2014**, *114*, 9219–9280; (b) Bering, L.; Antonchick, A. P. *Org. Lett.* **2015**, *17*, 3134–3137; (c) Ueda, M. Nishimura, K. Kashima, R. Ryu, I. *Synlett* **2012**, *23*, 1085–1089; (d) Xiao, T.; Li, L.; Lin, G.; Mao, Z. W.; Zhou, L. *Org. Lett.* **2014**, *16*, 4232–4235; (e) Wilkinson, M. C. *Org. Lett.* **2011**, *13*, 2232–2235; (f) Hu, W.; Lin, J. P.; Song, L. R.; Long, Y. Q. *Org. Lett.* **2015**, *17*, 1268–1271; (g) Li, X.; Gu, X.; Li, Y.; Li, P. *ACS Catal.* **2014**, *4*, 1897–1900; (h) Cantillo, D.; de Frutos, O.; Rincón, J. A.; Mateos, C.; Kappe, C. O. *Org. Lett.* **2014**, *16*, 896–899; (i) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem.* **2013**, 5769–5804; (j) Hartwing, J. F. *Nature* **2008**, *455*, 314–322; (k) Godula, K.; Sames, D. *Science* **2006**, *312*, 67–72; (l) Mkhaliid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890–931; (m) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174–238; (n) Daugulis, O.; Do, H. Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074–1086.
2. (a) Lee, J. M.; Park, E. J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2008**, *130*, 7824–7825; (b) Ohkubo, K.; Fujimoto, A.; Fukuzumi, S. *Chem. Commun.* **2011**, *47*, 8515–8517; (c) Du, F. T.; Ji, J. X. *Chem. Sci.* **2012**, *3*, 460–465; (d) Thirunavukkarasu, V.; S. Ackermann, L. *Org. Lett.* **2012**, *14*, 6206–6209; (e) Zhang, C.; Feng, P.; Jiao, N. *J. Am. Chem. Soc.* **2013**, *135*, 15257–15262; (f) Yuan, C.; Liang, Y.; Hernandez, T.; Berriochoa, A.; Houk, K. N.; Siegel, D. *Nature* **2013**, *499*, 192–196; (g) Adams, A. M.; Du Bois, J. *Chem. Sci.* **2014**, *5*,

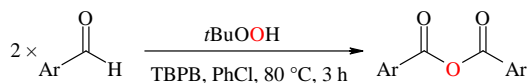
- 656–659; (h) Zhang, N.; Cheng, R.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *J. Org. Chem.* **2014**, *79*, 10581–10587; (i) Wang, Z. F.; Li, L.; Huang, Y. *J. Am. Chem. Soc.* **2014**, *136*, 12233–12236; (j) Wang, L.; Sha, W.; Dai, Q.; Feng, X.; Wu, W.; Peng, H.; Chen, B.; Cheng, J. *Org. Lett.* **2014**, *16*, 2088–2091; (k) Wan, J. P.; Zhou, Y.; Cao, S. *J. Org. Chem.* **2014**, *79*, 9872–9877.
3. (a) Zhang, Y.; Li, C. J.; *J. Am. Chem. Soc.* **2006**, *128*, 4242–4243; (b) Li, C. J. *Acc. Chem. Res.* **2009**, *42*, 335–344; (c) Zhang, C.; Xu, Z.; Zhang, L.; Jiao, N. *Angew. Chem. Int. Ed.* **2011**, *50*, 11088–11092; (d) He, C. Y.; Min, Q. Q.; Zhang, X. *Organometallics* **2012**, *31*, 1335–1340; (e) Fan, S.; Chen, Z.; Zhang, X. *Org. Lett.* **2012**, *14*, 4950–4953; (f) Mao, Z.; Wang, Z.; Xu, Z.; Huang, F.; Yu, Z.; Wang, R. *Org. Lett.* **2012**, *14*, 3854–3857; (g) Wertz, S.; Leifert, D.; Studer, A. *Org. Lett.* **2013**, *15*, 928–931; (h) Rajamanickam, S.; Majji, G.; Santra, S. K.; Patel, B. K. *Org. Lett.* **2015**, *17*, 5586–5589; (i) Sun, S.; Li, C.; Floreancig, P. E.; Lou, H.; Liu, L. *Org. Lett.* **2015**, *17*, 1684–1687; (j) Lee, H.; Yi, C. S. *Eur. J. Org. Chem.* **2015**, 1899–1904.
4. (a) Li, H.; Xie, J.; Xue, Q.; Cheng, Y.; Zhu, C. *Tetrahedron Lett.* **2012**, *53*, 6479–6482. (b) Shi, E.; Shao, Y.; Chen, S.; Hu, H.; Liu, Z.; Zhang, J.; Wan, X. *Org. Lett.* **2012**, *14*, 3384–3387; (c) Xue, Q.; Xie, J.; Xu, P.; Hu, K.; Cheng, Y.; Zhu, C. *ACS Catal.* **2013**, *3*, 1365–1368; (d) Majji, G.; Guin, S.; Gogoi, A.; Rout S. K.; Patel B. K. *Chem. Commun.* **2013**, *49*, 3031–3033; (e) Wu, X. F.; Gong, J. L.; Qi, X. *Org. Biomol. Chem.* **2014**, *12*, 5807–5817; (f) Siddaraju, Y.; Lamani, M.; Prabhu, K. R. *J. Org. Chem.* **2014**, *79*, 3856–3865; (g) Aruri, H.; Singh, U.; Sharma, S.; Gudup, S.; Bhogal, M.; Kumar, S.; Singh, D.; Gupta, V. K.; Kant, R.; Vishwakarma, R. A.; Singh, P.P. *J. Org. Chem.* **2015**, *80*, 1929–1936; (h) Yadav More, N.; Jeganmohan, M. *Org. Lett.* **2015**, *17*, 3042–3045; (i) Khatun, N.; Banerjee, A.; Santra, S. K.; Ali, W.; Patel, B. K. *RSC Adv.* **2015**, *5*, 36461–36466; (j) Banerjee, A.; Santra, S. K.; Khatun, N.; Ali, W.; Patel, B. K. *Chem. Commun.* **2015**, *51*, 15422–15425; (k) Majji, G.; Rajamanickam, S.; Khatun, N.; Santra, S. K.; Patel, B. K. *J. Org. Chem.* **2015**, *80*, 3440–3446; (l) Behera, A.; Ali, W.; Guin, S.; Khatun, N.; Mohanta, P. R.; Patel, B. K. *RSC Adv.* **2015**, *5*, 33334–33338; (m) Ali, W.; Behera, A.; Guin, S.; Patel, B. K. *J. Org. Chem.* **2015**, *80*, 5625–5632.
5. (a) Held, H.; Rengstl, A.; Mayer, D. *Acetic Anhydride and Mixed Fatty Acid Anhydrides: Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH,

- Weinheim, Germany, **2002**. (b) Ogliaruso, M. A.; Wolfe, J. F. *Synthesis of Carboxylic Acids, Esters and Their Derivatives*; John Wiley & Sons: New York, **1991**. pp 198–217.
6. (a) Rebek, J. Jr.; Feitler, D. *J. Am. Chem. Soc.* **1974**, *96*, 1606–1607; (b) Ogliaruso, M. A.; Wolfe, J. F. *Synthesis of Carboxylic Acids, Esters, and Their Derivatives*, Wiley: New York, **1991**; (c) Held, H.; Rengstl, A.; Mayer, D. *Acetic Anhydride and Mixed Fatty Acid Anhydrides: Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH: Weinheim, **2002**.
7. (a) Kocz, R.; Roestamadji, J.; Mobashery, S. *J. Org. Chem.* **1994**, *59*, 2913–2914; (b) Kazemi, F.; Sharghi, H.; Nasser, M. A. *Synthesis* **2004**, 205–207; (c) Kazemi, F.; Kiasat, A. R. *Phosphorus Sulfur* **2003**, *178*, 2287–2291; (d) Kazemi, F.; Kiasat, A. R.; Mombaini, B. *Synth. Commun.* **2007**, *37*, 3219–3223; (e) Kawamura, Y.; Sato, Y.; Horie, T.; Tsukayama, M. *Tetrahedron Lett.* **1997**, *38*, 7893–7896; (f) Keshavamurthy, K. S.; Vankar, Y. D.; Dhar, D. N. *Synthesis* **1982**, 506–508; (g) Clarke, P. A.; Kayaleh, N. E.; Smith, M. A.; Baker, J. R.; Bird, S. J.; Chan, C. *J. Org. Chem.* **2002**, *67*, 5226–5231; (h) Hu, Y. L.; Zhao, X. E.; Lu, M. *Bull. Chem. Soc. Ethiop.* **2011**, *25*, 255–262; (i) Kikukawa, K.; Kono, K.; Nagira, K.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1981**, *46*, 4413–4416; (j) Dhimitruka, I.; SantaLucia J., Jr. *Org. Lett.* **2006**, *8*, 47–50.
8. (a) Li, Y.; Xue, D.; Wang, C.; Liu, Z. T.; Xiao, J. *Chem. Commun.* **2012**, *48*, 1320–1322; (b) Khatun, N.; Santra, S. K.; Banerjee, A.; Patel, B. K. *Eur. J. Org. Chem.* **2015**, 1309–1313; (c) Saberi, D.; Shojaeyan, F.; Niknam, K. *Tetrahedron Lett.* **2016**, *57*, 566–569; (d) Nuree, Y.; Singha, R.; Ghosh, M.; Roy, P.; Ray, J. K. *Tetrahedron Lett.* **2016**, *57*, 1479–1482; (e) Singha, R.; Ghosh, M.; Nuree, Y.; Ray, J. K. *Tetrahedron Lett.* **2016**, *57*, 1325–1327.
9. Adib, M.; Peytam, F.; Zainali, M.; Zhu, L. G.; Wu, J. *Tetrahedron Lett.* **2015**, *56*, 4729–4732; Adib, M.; Soheilizad, M.; Rajai-Daryasarei, S.; Mirzaei, P. *Synlett* **2015**, *26*, 1101–1105; Adib, M.; Soheilizad, M.; Zhu, L. G.; Wu, J. *Synlett* **2015**, *26*, 177–182; Adib, M.; Janatian Ghazvini, H.; Soheilizad, M.; Saedi, S.; Tajbakhsh, M.; Amanlou, M. *Helv. Chim. Acta* **2015**, *98*, 1079–1086; Adib, M.; Sheikhi, E.; Azimzadeh, M. *Tetrahedron Lett.* **2015**, *56*, 1933–1936; Adib, M.; Sheikhi, E.; Haghshenas, P.; Rajai-Daryasarei, S.; Bijanzadeh, H. R.; Zhu, L. G. *Tetrahedron Lett.* **2014**, *55*, 4983–4986; Adib, M.; Sheikhi, E.; Rezaei, N.; Bijanzadeh, H. R.; Mirzaei, P. *Synlett* **2014**, *25*, 1331–1334.

10. **General procedure for the synthesis of benzoic anhydride (2a).** In a 5 mL sealed tube, TBPB (30 mol%, 0.051 g), and TBHP (70 wt% in H₂O, 0.6 mmol, 0.078 g) were added to a solution of benzaldehyde **1a** (0.5 mmol, 0.053 g), in chlorobenzene (0.75 mL). The resultant mixture was heated at 80 °C for 3 h. After reaction completion as indicated by TLC, the reaction mixture was cooled to room temperature and saturated NaHCO₃ (2 mL) was added. The product was extracted with EtOAc (2 × 3 mL). The combined organic extract was dried over Na₂SO₄ and the solvent removed under reduced pressure. The residue was purified by column chromatography using *n*-hexane-EtOAc (15:1) as eluent to afford **2a** as a white solid: ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (dd, *J* = 8.1, 7.8 Hz, 4H), 7.65 (t, *J* = 7.8 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 4H). ¹³C NMR (100.6 MHz, CDCl₃): δ = 128.9, 129.0, 130.5, 134.6, 162.4.
11. (a) Gan, L.; Huang, S.; Zhang, X.; Zhang, A.; Cheng, B.; Cheng, H.; Li, X.; Shang, G. *J. Am. Chem. Soc.* **2002**, *124*, 13384–13385; (b) Jones, C. M.; Burkitt, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 6946–6954; (c) Uyanik, M. Okamoto, H. Yasui, T. Ishihara, K. *Science* **2010**, *328*, 1376; (d) Feng, J.; Liang, S.; Chen, S. Y.; Zhang, J.; Fu, S. S.; Yu, X. Q. *Adv. Synth. Catal.* **2012**, *354*, 1287–1292; (e) Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. *Angew. Chem. Int. Ed.* **2012**, *51*, 3231–3235; (f) Li, H.; Xie, J.; Xue, Q.; Cheng, Y.; Zhu, C. *Tetrahedron Lett.* **2012**, *53*, 6479–6482; (g) Rout, S. K.; Guin, S.; Ali, W.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2014**, *16*, 3086–3089.

Metal free cross-dehydrogenative coupling of aryl aldehydes to give symmetrical carboxylic anhydrides promoted by the TBHP/*n*Bu₄PBr system

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Ar = C₆H₅, 2-CH₃C₆H₄, 3-CH₃C₆H₄, 4-CH₃C₆H₄, 15 examples
 2,5-(CH₃)₂C₆H₃, 2-CH₃OC₆H₄, 3-CH₃OC₆H₄, 51–86% yields
 4-CH₃OC₆H₄, 2,5-(CH₃O)₂C₆H₃,
 3,4-(CH₃O)₂C₆H₃, 1-naphthyl, 2-naphthyl,
trans-PhCH=CH-, 2-furyl, 2-thienyl

Research highlights

- Dual C–O bond formation *via* cross-dehydrogenative coupling reaction
- An efficient synthesis of symmetrical anhydrides under metal-free conditions
- TBHP/*n*Bu₄PBr as a novel and efficient catalytic system

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