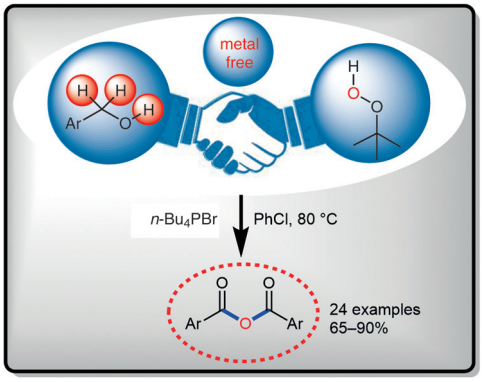
Synlett M. Adib, R. Pashazadeh Letter

TBHP/*n*-Bu_4PBr-Promoted Oxidative Cross-Dehydrogenative Coupling of Aryl Methanols: A Facile Synthesis of Symmetrical Carboxylic Anhydride Derivatives

Mehdi Adib*
Rahim Pashazadeh

School of Chemistry, College of Science, University of Tehran,
PO Box 14155-6455, Tehran, Iran
madib@khayam.ut.ac.ir



Received: 16.06.2017
Accepted after revision: 19.08.2017
Published online: 15.09.2017
DOI: 10.1055/s-0036-1590905; Art ID: st-2017-d0480-l

Abstract A transition-metal-free oxidative cross-dehydrogenative coupling reaction has been developed for the preparation of symmetrical carboxylic anhydrides through self-coupling dual C–O bond formations of aryl methanols. In the presence of a catalytic amount of tetrabutylphosphonium bromide (TBPB) as transfer agent and aqueous *tert*-butyl hydroperoxide (TBHP) as oxidant and reactant, methylene groups of aryl methanols were efficiently oxidized to C=O and coupled with the peroxide oxygen from TBHP to form a diverse array of symmetrical carboxylic anhydride derivatives.

Key words cross-dehydrogenative coupling, tetrabutylphosphonium bromide, *tert*-butyl hydroperoxide, aryl methanols, symmetrical carboxylic anhydrides

C–H bond activation and functionalization is attractive due to its atom- and step-economy.[1] Cross-dehydrogenative coupling (CDC) reactions for forming of a diverse array of various bonds such as C–C, C–O, C–N, C–P, and C–S are cornerstone reactions in organic chemistry.[2] Formation of C–O bonds has been achieved in the presence of transition-metal catalysts such as copper, iron, ruthenium, rhodium, iridium, and palladium in combination with various oxidants through activation of C–H bonds.[3] However, transition-metal-free-based CDC reactions for formation of C–O bonds are preferable due to their low cost and toxicity in comparison to transition-metal-catalyzed reactions that are less attractive for large-scale industrial applications.[4]

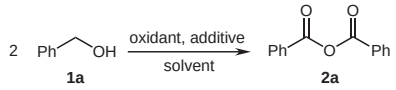
In recent years, the use of oxidants in CDC reactions, both as oxidant as well as reactant has been emerged as a preferred strategy for the construction of C–O and C=O bonds.[5] Among those oxidants, TBHP has received significant attention.[6] In this context, the use of alcohols as acylating agents has received attention.[7] Recent breakthroughs involving the CDC reaction of aldehydes via C–H oxidation and activation for the synthesis of symmetrical carboxylic anhydrides have been reported by Patel,[8a] Saberi,[8b] and Ray.[8c,d] In a continuation of our interest in generating heterocycles from readily available starting materials[9] and our recent studies on CDC reactions,[10] we have recently reported the TBHP/*n*-Bu_4PBr-promoted transformation of aryl aldehydes to symmetrical carboxylic anhydrides through metal-free CDC reaction.[11]

To the best of our knowledge, there is no report in the literature concerning the direct conversion of aryl methanols to their corresponding symmetrical carboxylic anhydrides. Herein, we present a novel metal-free oxidative self-coupling of aryl methanols using TBHP as oxidant and reactant to synthesize carboxylic anhydrides via CDC reaction.

To screen the reaction parameters, benzyl alcohol (**1a**) was selected as the model substrate, wherein we investigated the effect of different oxidants, additives, solvents, and temperature on the yield of the reaction (Table 1). According to the results, optimal conditions for the synthesis of benzoic anhydride (**2a**) from benzyl alcohol (**1a**) were determined to be 2.2 equivalents of TBHP as oxidant, 30 mol% of TBPB as additive, in chlorobenzene, at 80 °C for 2.5 hours (Table 1, entry 5).[12]

Based on the optimized conditions, we prepared a range of aromatic anhydrides **2** from aryl methanols **1** (Table 2). Benzyl alcohols containing neutral and electron-donating groups such as (one or more) Me, OMe, SMe, OEt, and OBu on the aryl ring gave the desired products **2a–n** in 75–90% yields (Table 2, entries 1–14). In addition, piperonol, 1,2-phenylenedimethanol, and naphthalene-2,3-diyldimethanol were also good reaction partners, providing the corre-

Table 1 Conditions Screening for the CDC Transformation of Benzyl Alcohol **1a** to Benzoic Anhydride **2a**[a]

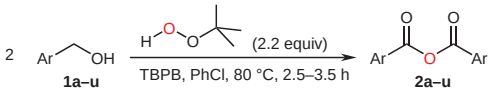


Entry	Oxidant (equiv)[b]	Additive (mol%)[b]	Solvent	Temp (°C)	Yield (%)[c]
1	TBHP[d] (2)	TBPB[e] (15)	PhCl	25	NR[f]
2	TBHP (2)	TBPB (15)	PhCl	50	35
3	TBHP (2)	TBPB (15)	PhCl	80	60
4	TBHP (2.2)	TBPB (15)	PhCl	80	75
5	TBHP (2.2)	TBPB (30)	PhCl	80	90
6	TBHP (2.2)	TBPB (30)	PhCl	100	75
7	TBHP (3)	TBPB (30)	PhCl	80	90
8	TBHP (2.2)	TBPB (40)	PhCl	80	90
9[g]	TBHP (2.2)	TBPB (30)	PhCl	80	85
10	TBHP (2.2)	NBS[h] (30)	PhCl	80	30
11	TBHP (2.2)	TBAB[i] (30)	PhCl	80	82
12	TBHP (2.2)	Aliquat 336[j] (30)	PhCl	80	45
13	TBHP (2.2)	I_2 (30)	PhCl	80	30
14	TBHP (2.2)	KI (30)	PhCl	80	NR
15	TBHP (2.2)	CuI (30)	PhCl	80	NR
16	$K_2S_2O_8$ (2.2)	TBPB (30)	PhCl	80	NR
17	$(NH_4)_2S_2O_8$ (2.2)	TBPB (30)	PhCl	80	NR
18	BPO[k] (2.2)	TBPB (30)	PhCl	80	65
19	H_2O_2[l] (2.2)	TBPB (30)	PhCl	80	NR
20	TBHP (2.2)	TBPB (30)	$PhCH_3$	80	40
21	TBHP (2.2)	TBPB (30)	DCE	80	50
22	TBHP (2.2)	TBPB (30)	MeCN	80	NR
23	TBHP (2.2)	TBPB (30)	DMSO	80	NR
24	TBHP (2.2)	TBPB (30)	H_2O	80	NR
25	TBHP (2.2)	TBPB (30)	EtOAc	80	trace
26	–	TBPB (30)	PhCl	80	NR
27	TBHP (2.2)	–	PhCl	80	NR

[a] Reaction conditions: **1a** (0.4 mmol), solvent (1.0 mL) for 2.5 h.
[b] With respect to **1a**.
[c] Isolated yields.
[d] 70 wt% *t*-BuOOH in H_2O.
[e] Tetrabutylphosphonium bromide.
[f] NR = no reaction.
[g] Reaction time 6 h.
[h] *N*-Bromosuccinimide.
[i] Tetrabutylammonium bromide.
[j] Tricaprylmethylammonium chloride.
[k] Benzoyl peroxide.
[l] 30 wt% H_2O_2 in H_2O.

sponding products **2o**, **2p**, and **2q** in 84%, 87%, and 65% yields, respectively (Table 2, entries 15–17). Furthermore, naphthylmethanols (**1r** and **1s**) and anthracen-9-ylmethanol (**1t**) as well as heteroaryl methanols such as 2-thienylmethanol (**1u**), 3-thienylmethanol (**2v**), and 2-furylmethanol (**1w**) were successfully applied to this conversion and provided the corresponding products **2r–w** in 74–90% yields (Table 2, entries 18–23). Additionally, when 3-phenyl-2-propen-1-ol (**1x**) was tested, the reaction well proceeded to provide cinnamic anhydride **2x** in (68%) yield (Table 2, entry 24). However, primary aliphatic alcohols 2-methylpropane-1-ol (**1aa**), *n*-butanol (**1ab**), and 2-phenylethanol (**1ac**) did not give the corresponding anhydrides **2aa–ac** under these conditions (Table 2, entries 25–27).

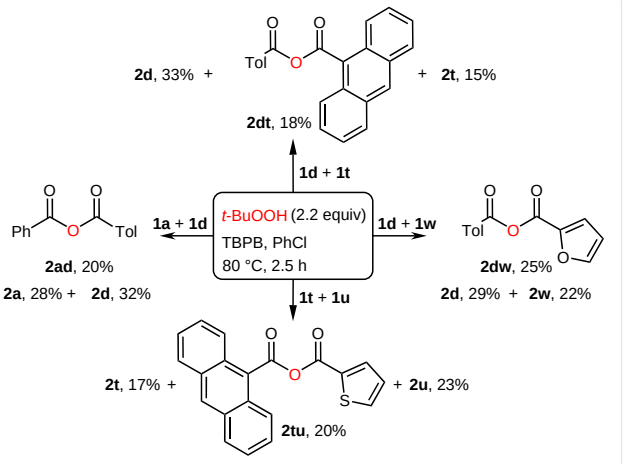
Table 2 Substrate Scope for the Synthesis of Carboxylic Anhydrides **2a–u** under the Optimized CDC Metal-Free Reactions[a]



Entry	1	Ar or RCH_2OH	Time (h)	2	Yield (%)[b]
1	**1a**	Ph	2.5	**2a**	90
2	**1b**	2-MeC_6H_4	3	**2b**	80
3	**1c**	3-MeC_6H_4	2.5	**2c**	86
4	**1d**	4-MeC_6H_4	2.5	**2d**	82
5	**1e**	2,5-$Me_2C_6H_3$	3	**2e**	83
6	**1f**	2-$MeOC_6H_4$	3.5	**2f**	78
7	**1g**	3-$MeOC_6H_4$	2.5	**2g**	87
8	**1h**	4-$MeOC_6H_4$	3	**2h**	82
9	**1i**	4-$MeSC_6H_4$	3	**2i**	77
10	**1j**	4-$EtOC_6H_4$	3.5	**2j**	81
11	**1k**	4-*n*-$BuOC_6H_4$	3.5	**2k**	76
12	**1l**	2,5-$(MeO)_2C_6H_3$	3.5	**2l**	75
13	**1m**	3,4-$(MeO)_2C_6H_3$	3	**2m**	83
14	**1n**	3,4,5-$(MeO)_3C_6H_2$	3.5	**2n**	76
15	**1o**	3,4-$(OCH_2O)C_6H_3$	3.5	**2o**	84
16	**1p**	2-$(HOCH_2)C_6H_4$	3	**2p**	87
17	**1q**	3-$(HOCH_2)$-2-naphthyl	3.5	**2q**	65
18	**1r**	1-naphthyl	2.5	**2r**	90
19	**1s**	2-naphthyl	3	**2s**	84
20	**1t**	9-anthracyl	3	**2t**	75
21	**1u**	2-thienyl	3	**2u**	83
22	**1v**	3-thienyl	3	**2v**	80
23	**1w**	2-furyl	3.5	**2w**	74
24	**1x**	*trans*-PhCH=CH–	3.5	**2x**	68
25	**1aa**	Me_2CHCH_2OH	3.5	**2aa**	NR
26	**1ab**	$Me(CH_2)_3OH$	3.5	**2ab**	NR
27	**1ac**	$Ph(CH_2)_2OH$	3.5	**2ac**	NR

[a] Reaction conditions: aryl methanol (**1**, 0.4 mmol), TBHP (1 mmol), TBPB (30 mol%), in PhCl (1.0 mL).
[b] Isolated yields.

Inspired by these results, we turned our attention to the construction of unsymmetrical anhydrides and this was found to perform well using a mixture of aryl methanols under the standard conditions (Scheme 1). In these transformations, symmetrical anhydrides such as **2a**, **2d**, **2t**, **2u**, and **2w** were obtained by self-coupling of the aryl methanols; whereas unsymmetrical anhydrides such as **2ad** (20%), **2dt** (18%), **2dw** (25%), and **2tu** (20%) were formed by cross-coupling of **1a** with **1d**, **1d** with **1t**, **1d** with **1w**, and **1t** with **1u**, respectively.

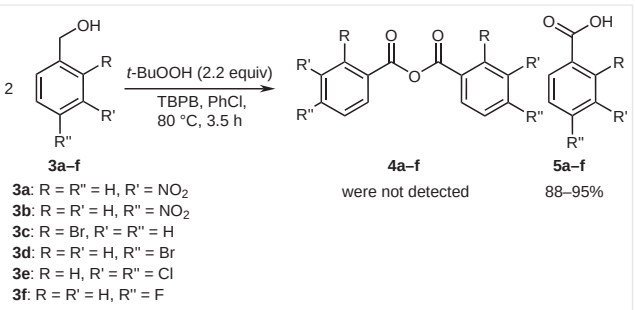


2a, **2d**, **2t**, **2u** and **2w**: Symmetrical carboxylic anhydrides resulting from the self-coupling of aryl methanols (see Table 2)
2ad, **2dt**, **2dw** and **2tu**: Unsymmetrical carboxylic anhydrides resulting from the cross-coupling of the two aryl methanols

Scheme 1 Synthesis of unsymmetrical carboxylic anhydrides

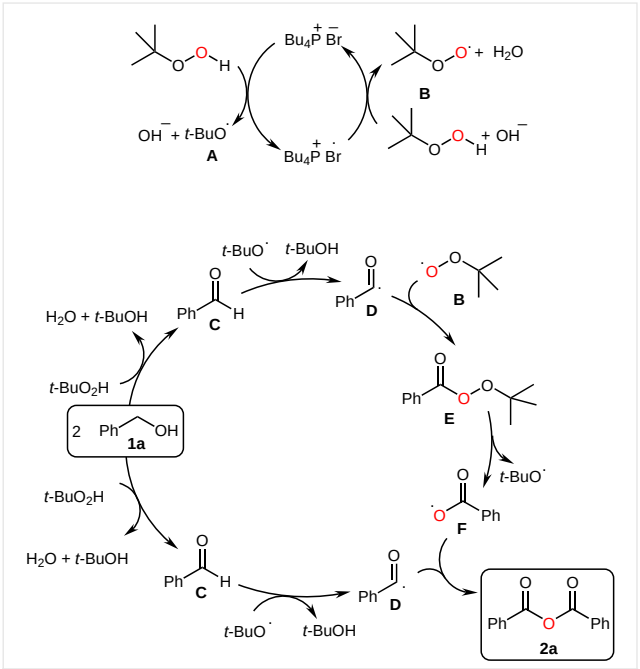
To further explore the substrate scope of this reaction, electron-withdrawing groups on the benzyl alcohol such as 3-NO_2, 4-NO_2, 2-Br, 4-Br, 3,4-Cl_2, and 4-F were reacted with TBHP according to the optimized conditions in Table 1 (entry 5). However, the desired benzoic anhydrides **4a–f** were not obtained and only the corresponding carboxylic acids **5a–f** were observed (Scheme 2).

Based on these considerations, a plausible mechanism is proposed for the oxidative self-coupling process (Scheme 3). At the first stage of this oxidation reaction, *n*-Bu_4PBr may react with TBHP to give *tert*-butoxy **A** and *tert*-butyl peroxy **B** radicals.[6f,8a,13] Next, benzyl alcohol **1a** is oxidized by TBHP to form benzaldehyde **C**. The formed *tert*-butoxy radical **A** may abstract a hydrogen atom from benzaldehyde **C** to generate the corresponding acyl radical **D**, which may further react with *tert*-butyl peroxy radical **B** to afford *tert*-butyl peroxybenzoate **E**[6f,13a] (detected by GC–MS analysis of the reaction mixture; see Figure S1 in the Supporting Information). Intermediate **E** undergoes thermal cleavage owing to a weak O–O bond to generate the benzoyloxy radical **F** and re-introduce *tert*-butoxy radical **A** to the reaction cycle. Ultimately, the acyl radical **D** and benzoyloxy radical **F** couple to form the desired benzoic anhydride **2a**.



3a: R = R'' = H, R' = NO_2
3b: R = R' = H, R'' = NO_2
3c: R = Br, R' = R'' = H
3d: R = R' = H, R'' = Br
3e: R = H, R' = R'' = Cl
3f: R = R' = H, R'' = F

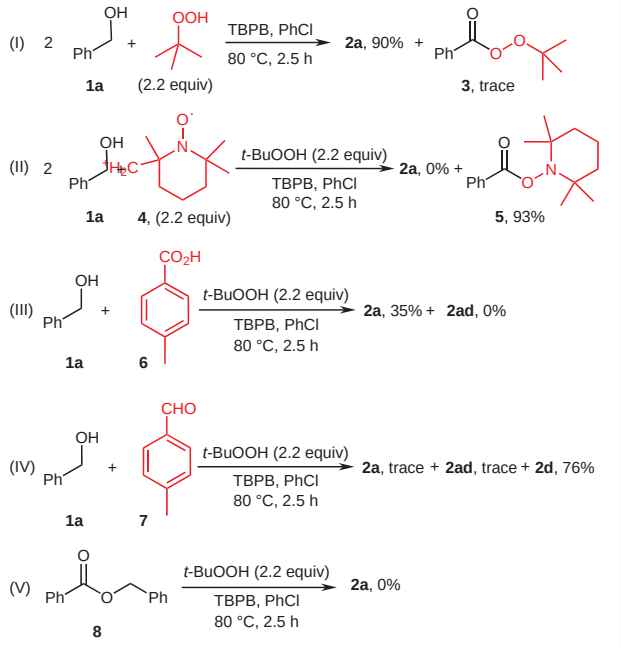
Scheme 2 Reaction of aryl methanols having electron-withdrawing substituents



Scheme 3 Proposed mechanism of the reaction

To investigate the reaction mechanism, control experiments were conducted, as shown in Scheme 4. Exclusive formation of benzoic anhydride **2a** was observed for this oxidative CDC reaction of **1a** indicating a high degree of selectivity, while *tert*-butyl peresters **3** have been reported to be formed in Bu_4NI-catalyzed metal-free oxidation of aldehydes or aryl methanols by TBHP[14] (eq. I). When 2,2,6,6-tetramethylpiperidine *N*-oxide **4** (TEMPO, 2.2 equiv), as a radical scavenger, was added to the reaction mixture of benzyl alcohol **1a** under the optimized conditions, 2,2,6,6-tetramethylpiperidino benzoate **5** was obtained in 93% yield and benzoic anhydride **2a** was not detected (eq. II). By adding 4-methylbenzoic acid **6** to the reaction mixture of **1a**, the yield of anhydride **2a** decreased to 35%, and the unsymmetrical anhydride **2ad** was not detected (eq. III). When 4-methylbenzaldehyde **7** was added to the reaction mixture

of **1a**, the corresponding anhydride **2d** was observed as the major product (eq. IV). We also found that, in this oxidation transformation, benzyl benzoate **8** could not be oxidized with TBHP to afford the desired product **2a** under the standard conditions (eq. V).[8a]



Scheme 4 Control experiments

In conclusion, we have developed a CDC reaction for the preparation of symmetrical carboxylic anhydrides. This reaction was performed using the TBHP/*n*-Bu_4PBr system to oxidize and catalyze self-coupling of aryl methanols and construct C–O and C=O bonds in the carboxylic anhydride skeleton. TBHP acted as the oxidant and oxygen source to construct the C–O and C=O bonds. The attractive features of this protocol are the use of aryl methanols in place of aldehydes and carboxylic acid derivatives, simple operation, moderate temperature, broad substrate scope, no requirement for transition-metal catalysts, and high yields of the products. To the best of our knowledge, this is the first report on the synthesis of carboxylic anhydrides using aryl methanols as starting materials.

Funding Information

This research was supported by the Research Council of University of Tehran.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1590905.

References and Notes

(1) (a) Dyker, G. *Handbook of C–H Transformations: Applications in Organic Synthesis*; Wiley-VCH: Weinheim, **2005**. (b) Yu, J. Q.; Shi, Z. J. *C–H Activation*; Springer: Berlin, **2010**. (c) Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 11212. (d) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J. Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094. (e) Xu, L. M.; Li, B. J.; Yang, Z.; Shi, Z. J. *Chem. Soc. Rev.* **2010**, *39*, 712. (f) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (g) Wencel-Delord, J.; Droge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740. (h) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (i) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. (j) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936. (k) Engle, K. M.; Mei, T. S.; Wasa, M.; Yu, J. Q. *Acc. Chem. Res.* **2012**, *45*, 788. (l) Dyker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1698. (m) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (n) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.

(2) (a) Li, Z.; Li, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 11810. (b) Li, Z.; Li, C. J. *Org. Lett.* **2004**, *6*, 4997. (c) Zhao, L.; Li, C. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 7075. (d) Li, Z.; Li, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 6968. (e) Li, Z.; Li, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 3672. (f) Zhang, Y.; Li, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 4242. (g) Li, Z.; Li, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 56. (h) Deng, G.; Zhao, L.; Li, C. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 6278. (i) Zhang, Y.; Feng, J.; Li, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 2900. (j) Li, C. J. *Acc. Chem. Res.* **2009**, *42*, 335. (k) Correia, C. A.; Li, C. J. *Adv. Synth. Catal.* **2010**, *352*, 1446. (l) Girard, S. A.; Knauber, T.; Li, C. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 74. (m) Shi, Z. J.; Li, B. J. *Chem. Soc. Rev.* **2012**, *41*, 5588. (n) Zhang, C.; Tang, C. H.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3464. (o) Sun, C. L.; Li, B. J.; Shi, Z. J. *Chem. Rev.* **2011**, *111*, 1293. (p) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780. (q) Yang, Y.; Chen, Z.; Rao, Y. *Chem. Commun.* **2014**, *50*, 15037. (r) Xiang, C. B.; Bian, Y. J.; Mao, X. R.; Huang, Z. Z. *J. Org. Chem.* **2012**, *77*, 7706.

(3) (a) Yoneyama, T.; Crabtree, R. H. *J. Mol. Catal. A: Chem.* **1996**, *108*, 35. (b) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300. (c) Desai, L. V.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9542. (d) Giri, R.; Liang, J.; Lei, J. G.; Li, J. J.; Wang, D. H.; Chen, X.; Naggar, I. C.; Guo, C.; Foxman, B. M.; Yu, J. Q. *Angew. Chem. Int. Ed.* **2005**, *44*, 7420. (e) Chen, X.; Hao, X. S.; Goodhue, C. E.; Yu, J. Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790. (f) Ye, Z.; Wang, W.; Luo, F.; Zhang, S.; Cheng, J. *Org. Lett.* **2009**, *11*, 3974. (g) Ali, W.; Rout, S. K.; Guin, S.; Modi, A.; Banerjee, A.; Patel, B. K. *Adv. Synth. Catal.* **2015**, *357*, 515. (h) Wu, Y.; Wang, J.; Mao, F.; Kwong, F. Y. *Chem. Asian J.* **2014**, *6*, 26.

(4) (a) Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 5331. (b) Shi, E.; Shao, Y.; Chen, S.; Hu, H.; Liu, Z.; Zhang, J.; Wan, X. *Org. Lett.* **2012**, *14*, 3384. (c) Siddaraju, Y.; Lamani, M.; Prabhu, K. R. *J. Org. Chem.* **2014**, *79*, 3856. (d) Rajamanickam, S.; Majji, G.; Santra, S. K.; Patel, B. K. *Org. Lett.* **2015**, *17*, 5586. (e) Majji, G.; Guin, S.; Gogoi, A.; Rout, S. K.; Patel, B. K. *Chem. Commun.* **2013**, *49*, 3031. (f) Yuan, Y.; Hou, W.; Zhang-Negrerie, D.; Zhao, K.; Du, Y. *Org. Lett.* **2014**, *16*, 5410. (g) Zheng, Z.; Dian, L.; Yuan, Y.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *J. Org. Chem.* **2014**, *79*, 7451.

(5) (a) Kalyani, D.; Sanford, M. S. *Org. Lett.* **2005**, *7*, 4149. (b) Gogoi, A.; Sau, P.; Ali, W.; Guin, S.; Patel, B. K. *Eur. J. Org. Chem.* **2016**, 1449. (c) Zhang, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 28. (d) Wang, Y. F.; Chen, H.; Zhu, X.; Chiba, S. *J. Am. Chem. Soc.* **2012**, *134*, 11980. (e) Thirunavukkarasu, V. S.; Ackermann, L. *Org. Lett.* **2012**, *14*, 6206. (f) Du, F. T.; Ji, J. X. *Chem. Sci.* **2012**, *3*, 460. (g) Yuan, C.; Liang, Y.; Hernandez, T.; Berriochoa, A.; Houk,

K. N.; Siegel, D. *Nature (London, U.K.)* **2013**, *499*, 192. (h) Poladura, B.; Martínez-Castañeda, Á.; Rodríguez-Solla, H.; Llavona, R.; Concellón, C.; del Amo, V. *Org. Lett.* **2013**, *15*, 2810. (i) Liang, Y. F.; Wang, X.; Yuan, Y.; Liang, Y.; Li, X.; Jiao, N. *ACS Catal.* **2015**, *5*, 6148.

(6) (a) Rout, S. K.; Guin, S.; Banerjee, A.; Khatun, N.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2013**, *15*, 4106. (b) Wu, Y.; Choy, P. Y.; Mao, F.; Kwong, F. Y. *Chem. Commun.* **2013**, *49*, 689. (c) Majji, G.; Guin, S.; Rout, S. K.; Behera, A.; Patel, B. K. *Chem. Commun.* **2014**, *50*, 12193. (d) Banerjee, A.; Santra, S. K.; Khatun, N.; Ali, W.; Patel, B. K. *Chem. Commun.* **2015**, *51*, 15422. (e) Ouyang, X. H.; Song, R. J.; Li, Y.; Liu, B.; Li, J. H. *J. Org. Chem.* **2014**, *79*, 4582. (f) Rout, S. K.; Guin, S.; Ali, W.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2014**, *16*, 3086. (g) Gogoi, A.; Modi, A.; Guin, S.; Rout, S. K.; Das, D.; Patel, B. K. *Chem. Commun.* **2014**, *50*, 10445.

(7) (a) Nordstrøm, L. U.; Vogt, H.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 17672. (b) Xiao, F.; Shuai, Q.; Zhao, F.; Basle, O.; Deng, G.; Li, C. J. *Org. Lett.* **2011**, *13*, 1614. (c) Xiao, F.; Liu, Y.; Tang, C.; Deng, G. J. *Org. Lett.* **2012**, *14*, 984. (d) Fu, Z.; Lee, J.; Kang, B.; Hong, S. H. *Org. Lett.* **2012**, *14*, 6028. (e) Kang, B.; Fu, Z.; Hong, S. H. *J. Am, Chem. Soc.* **2013**, *135*, 11704. (f) Wang, N.; Zou, X.; Ma, J.; Li, F. *Chem. Commun.* **2014**, *50*, 8303. (g) Omuraa, R.; Fujiyaa, A.; Yamaguchia, E.; Tadaa, N.; Miurab, T.; Itoh, A. *Synthesis* **2016**, *48*, 3971.

(8) (a) Khatun, N.; Santra, S. K.; Banerjee, A.; Patel, B. K. *Eur. J. Org. Chem.* **2015**, 1309. (b) Saberi, D.; Shojaeyan, F.; Niknam, K. *Tetrahedron Lett.* **2016**, *57*, 566. (c) Nuree, Y.; Singha, R.; Ghosh, M.; Roy, P.; Ray, J. K. *Tetrahedron Lett.* **2016**, *57*, 1479. (d) Singha, R.; Ghosh, M.; Nuree, Y.; Ray, J. K. *Tetrahedron Lett.* **2016**, *57*, 1325.

(9) (a) Adib, M.; Ayashi, N.; Heidari, F.; Mirzaei, P. *Synlett* **2016**, *27*, 1738. (b) Adib, M.; Sheikhi, E.; Yazzaf, R.; Bijanzadeh, H. R.; Mirzaei, P. *Tetrahedron Lett.* **2016**, *57*, 841. (c) Adib, M.; Yasaei, Z.; Mirzaei, P. *Synlett* **2016**, *27*, 383. (d) Adib, M.; Zainali, M.; Kim, I. *Synlett* **2016**, *27*, 1844. (e) Adib, M.; Janatian Ghazvini, H.; Soheilizad, M.; Saeedi, S.; Tajbakhsh, M.; Amanlou, M. *Helv. Chim. Acta* **2015**, *98*, 1079. (f) Adib, M.; Soheilizad, M.; Rajai-Daryasarei, S.; Mirzaei, P. *Synlett* **2015**, *26*, 1101. (g) Adib, M.; Soheilizad, M.; Zhu, L. G.; Wu, J. *Synlett* **2015**, *26*, 177. (h) Adib, M.; Bayanati, M.; Soheilizad, M.; Janatian Ghazvini, H.; Tajbakhsh, M.; Amanlou, M. *Synlett* **2014**, *25*, 2918.

(10) (a) Adib, M.; Pashazadeh, R.; Rajai-Daryasarei, S.; Kabiri, R.; Gohari, S. J. A. *Synlett* **2016**, *27*, 2241. (b) Adib, M.; Rajai-Daryasarei, S.; Pashazadeh, R.; Tajik, M.; Mirzaei, P. *Tetrahedron Lett.* **2016**, *57*, 3701. (c) Adib, M.; Pashazadeh, R.; Rajai-Daryasarei, S.; Kabiri, R.; Jahani, M. *RSC Adv.* **2016**, *6*, 110656.

(11) Adib, M.; Pashazadeh, R.; Rajai-Daryasarei, S.; Mirzaei, P.; Gohari, S. J. A. *Tetrahedron Lett.* **2016**, *57*, 3071.

(12) **General Procedure for the Synthesis of Benzoic Anhydride (2a)**

In a 5 mL sealed tube, TBPB (30 mol%, 0.041 g) and TBHP (70 wt% in H_2O, 1.0 mmol, 0.131 g) were added to a solution of benzyl alcohol (**1a**, 0.4 mmol, 0.043 g) in chlorobenzene (1 mL). The resultant mixture was heated at 80 °C for 2.5 h. After completion of the reaction, as indicated by TLC monitoring, the reaction mixture was cooled to ambient temperature and sat. $NaHCO_3$ (2 mL) was added. The product was extracted with EtOAc (2 × 3 mL). The combined organic phases were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography using *n*-hexane–EtOAc (15:1) as eluent to afford pure product **2a** as a white solid (yield 90%); mp 44–45 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.55 (t, *J* = 7.6 Hz, 4 H), 7.70 (t, *J* = 7.5 Hz, 2 H), 8.18 (d, *J* = 7.8 Hz, 4 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 128.8, 128.9, 130.5, 134.6, 162.4.

(13) (a) Jones, C. M.; Burkitt, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 6946. (b) Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K. *Science* **2010**, *328*, 1376. (c) Feng, J.; Liang, S.; Chen, S. Y.; Zhang, J.; Fu, S. S.; Yu, X. Q. *Adv. Synth. Catal.* **2012**, *354*, 1287. (d) Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. *Angew. Chem. Int. Ed.* **2012**, *51*, 3231. (e) Li, H.; Xie, J.; Xue, Q.; Cheng, Y.; Zhu, C. *Tetrahedron Lett.* **2012**, *53*, 6479. (f) Gan, L.; Huang, S.; Zhang, X.; Zhang, A.; Cheng, B.; Cheng, H.; Li, X.; Shang, G. *J. Am. Chem. Soc.* **2002**, *124*, 13384.

(14) (a) Wei, W.; Zhang, C.; Xu, Y.; Wan, X. *Chem. Commun.* **2011**, *47*, 10827. (b) Zhang, H.; Dong, D. Q.; Hao, S. H.; Wang, Z. L. *RSC Adv.* **2016**, *6*, 8465.