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Ceric Ammonium Nitrate (CAN) Promoted Pd^{II}-Catalyzed Substrate-Directed *o*-Benzoxylation and Decarboxylative *o*-Aroylation

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Inexpensive ceric ammonium nitrate (CAN) is an efficient oxidant for the Pd-catalyzed substrate-directed *o*-benzoxylation and decarboxylative *o*-aroylation processes. In the presence of CAN, the reaction of directing arenes with carboxylic acids resulted in *o*-benzoxylated products, whereas a decarboxylative *o*-aroylation occurred by using α-keto acids, which led to the formation of *o*-aroylation products.

Introduction

The C–O bond formation reaction that proceeds through a C–H bond functionalization to give an ester has led to a resurgence of transition-metal-catalyzed reactions.[1] In this context, directing[2] and nondirecting[3] cross-dehydrogenative coupling (CDC) reactions are the most preferred approaches because of their step and atom economy. In addition to carboxylic acids,[1a,1b,2a–2c,2e] aroyl peroxides,[1c] acyl chlorides,[1g] acid anhydrides,[1k] aldehydes,[2d] alkylbenzenes,[2d] terminal alkenes,[1h] and terminal alkynes[1h] have been employed as *o*-benzoxy surrogates. A carboxylic acid has a propensity to form a metal complex, thereby rendering the metal inactive and inhibiting the progress of a reaction. To overcome this problem, a modified carboxylate source such as $PhI(OCOR)_2$ has been employed by Sanford[1a] as well as others.[1b] The combinations of $AgSbF_6/(NH_4)_2S_2O_8$,[2a,2b] CuI/Ag_2CO_3,[2c] and $P(Cy)_3 \cdot HBF_4/CuI$[2e] (Cy = cyclohexyl) along with metal catalysts such as Ru, Pd, and Rh have, in part, obviated the problems associated with their direct use. No doubt these modifications have improved the yields, but they are economically unviable. Thus, the lack of a cost-effective and generalized strategy for an *o*-benzoxylation that involves a range of directing groups leaves an ample opportunity to devise an alternative approach.

A typical substrate-directed transition-metal-catalyzed *o*-benzoxylation proceeds through a cyclometallation, oxidative addition, or ligand exchange followed by a reductive elimination. For a ligand exchange path, the metal is in its reduced state and needs to be reoxidized to maintain the catalytic cycle, which is often done with the aid of stoichiometric amounts of sacrificial terminal oxidants or other additives. Ceric ammonium nitrate (CAN), a one-electron oxidant, has been employed for various functional group transformations[4] and in the syntheses of heterocycles.[5] In spite of its immense applications as an oxidizing agent, its use as a terminal oxidant in palladium-catalyzed processes is completely unexplored. In continuation of our efforts with regard to transition-metal-catalyzed substrate-directed C–H functionalizations,[1h,6,12a] we have explored the use of CAN as a terminal oxidant. The reduction potentials of well-known oxidants that are used for decarboxylative *o*-aroylation and *o*-benzoxylation reactions are +0.80 V for Ag^I/Ag^0 and +2.01 V for $S_2O_8^{2-}/SO_4^{2-}$. In comparison, the reduction potential of Ce^{IV}/Ce^{III} is +1.61 V, which is between that of Ag^I/Ag^0 and $S_2O_8^{2-}/SO_4^{2-}$. Thus, Ce^{IV}/Ce^{III} is moderately oxidizing in nature, and as a single-electron oxidant, it may be capable of forming a carboxy radical from a carboxylic acid and an aroyl radical through a carboxy radical from an α-keto acid.

Results and Discussion

To the best of our knowledge, 2-arylbenzothiazole has never been *o*-benzoxylated through a C–H bond functionalization, however, it has been *ortho*-functionalized by using Pd catalysts.[6a,6b] To test the efficacy of CAN as an oxidant, a CDC reaction between 2-phenylbenzothiazole (**1**, 1 equiv.) and benzoic acid (**a**, 1.2 equiv.) was carried out by using $Pd(OAc)_2$ (5 mol-%) and CAN (1 equiv.) in toluene (2.5 mL) at 110 °C. The expected mono-*o*-benzoxylated product **1a** was obtained in 38% isolated yield. In addition to spectroscopic analysis for the characterization of the product, the structure of **1a** was further confirmed by using XRD analysis (see Figure 1). Fascinated by this preliminary success, we assessed other reaction parameters such as solvent, oxidant, catalyst, and amounts to achieve the best

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possible yield. Of the optimization results (see Table 1), the conversion of 2-phenylbenzothiazole (**1**, 1 equiv.) into *o*-benzoxylated product **1a** was best achieved by using benzoic acid (1.2 equiv.) and CAN (1.5 equiv.) in the presence of $Pd(OAc)_2$ (5 mol-%) in a mixture of 1,2-dichloroethane (DCE)/CH_3CN (5:1, 3 mL) at 110 °C. The addition of CH_3CN was necessary to make the medium homogeneous, thereby improving the yield (71%, see Table 1). When the reaction was carried out with 2 equiv. of benzoic acid for a longer period of time (17 h), trace amounts (11%) of dibenzoxylated product **1aa** were observed.

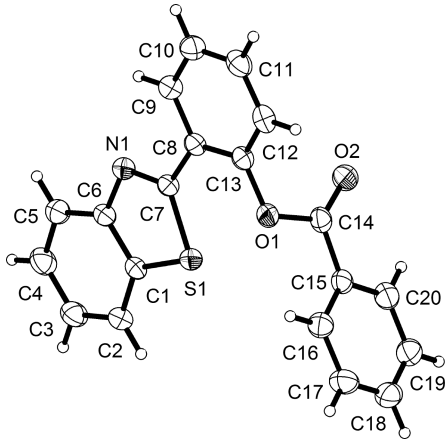
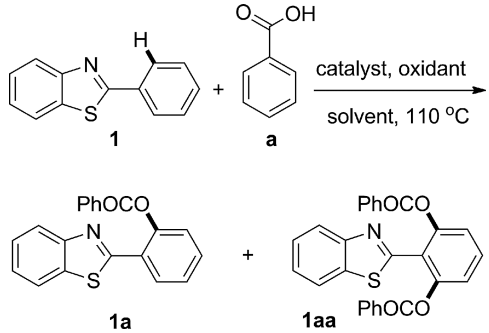


Figure 1. ORTEP view of **1a**.[16]

Encouraged by the efficacy of CAN as an oxidant, we further implemented the esterification strategy to the coupling between 2-phenylbenzothiazole and a series of carboxylic acids. This strategy was well-suited for a variety of aromatic acids that contained electron-donating and -withdrawing substituents. Aromatic acids that have electron-donating groups such as *p*-Me, *p*-OMe, and *o*-OMe (i.e., **b**, **c**, and **d**, respectively) provided the corresponding *o*-benzoxylated products **1b**, **1c**, and **1d** in good to moderate yields (see Scheme 1). Aromatic acids that contained moderately and strongly electron-withdrawing substituents such as *p*-Cl, *p*-NO_2, and *o*-NO_2 (i.e., **e**, **f**, and **g**) afforded the corresponding *o*-benzoxylated products **1e**, **1f**, and **1g** in 74, 80, and 83% yields respectively (see Scheme 1). A similar trend in reactivity was observed for di- and trisubstituted aromatic acids that contained electron-withdrawing substituents such as 2,6-dichloro and 2,4,5-trifluoro (i.e., **h** and **i**), and these carboxylic acids afforded their corresponding *o*-benzoxylated products **1h** and **1i** in decent yields (see Scheme 1). Fused aromatic acid **j** also afforded a good yield of *o*-carboxylated product **1j**. The oxidant CAN was also amenable to the α,β-unsaturated system *trans*-cinnamic acid (**k**) and provided a moderate yield (57%) of *o*-functionalized product **1k**. The efficiency of the coupling reaction was poor for aliphatic carboxylic acids, which may be a result of the instability of the in situ generated aliphatic carboxy radicals. Phenylacetic acid (**l**), propanoic acid (**m**), and pivalic acid (**n**) underwent the CDC reaction to afford *o*-carboxylated products **1l**, **1m**, and **1n** in 48, 45, and 34% yield, respectively.

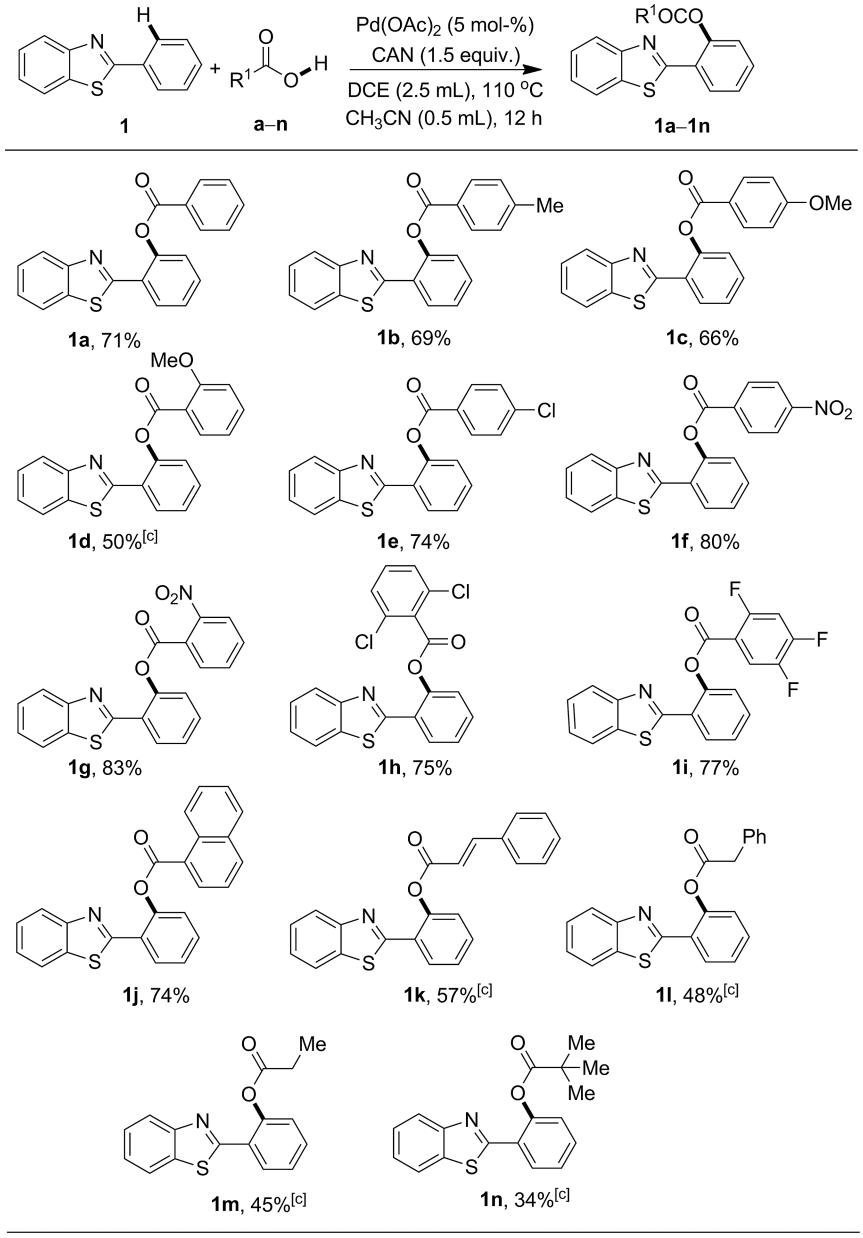
Table 1. Screening of reaction conditions for *o*-benzoxylation.



Entry	Catalyst [mol-%]	Solvent	Oxidant	% Yield **1a**/**1aa**[a,b]
1	$Pd(OAc)_2$ (5.0)	toluene	CAN	38
2	$Pd(OAc)_2$ (5.0)	*o*-xylene	CAN	10
3	$Pd(OAc)_2$ (5.0)	CH_3CN	CAN	0[c]
4	$Pd(OAc)_2$ (5.0)	1,4-dioxane	CAN	0[c]
5	$Pd(OAc)_2$ (5.0)	DMF[d]	CAN	0[c]
6	$Pd(OAc)_2$ (5.0)	DMSO[d]	CAN	0[c]
7	$Pd(OAc)_2$ (5.0)	DCE	CAN	56
8	$Pd(OAc)_2$ (10.0)	DCE	CAN	62
9	$Pd(TFA)_2$ (5.0)	DCE	CAN	41
10	$PdCl_2$ (5.0)	DCE	CAN	43
11	$PdBr_2$ (5.0)	DCE	CAN	48
12	$Pd(OAc)_2$ (5.0)	DCE	CAN	67[e]
13	$Pd(OAc)_2$ (5.0)	DCE	oxone	0[c]
12	$Pd(OAc)_2$ (5.0)	DCE	Ag_2CO_3/CuI	0[c]
13	$Pd(OAc)_2$ (5.0)	DCE	$K_2S_2O_8$	0[c]
14	$Pd(OAc)_2$ (5.0)	DCE/CH_3CN	CAN	71[e,f]
15	$Pd(OAc)_2$ (5.0)	DCE/CH_3CN	CAN	62:11[g]

[a] Reagents and conditions: 2-arylbenzothiazole (0.5 mmol), benzoic acid (0.60 mmol), and oxidant (0.5 mmol) at 110 °C for 12 h. [b] Isolated yield. [c] Complete recovery of starting materials. [d] DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide. [e] CAN (0.75 mmol) was used. [f] DCE/CH_3CN (5:1, total 3 mL) was used. [g] Benzoic acid (1 mmol) and CAN (1 mmol) were used at 110 °C for 17 h.

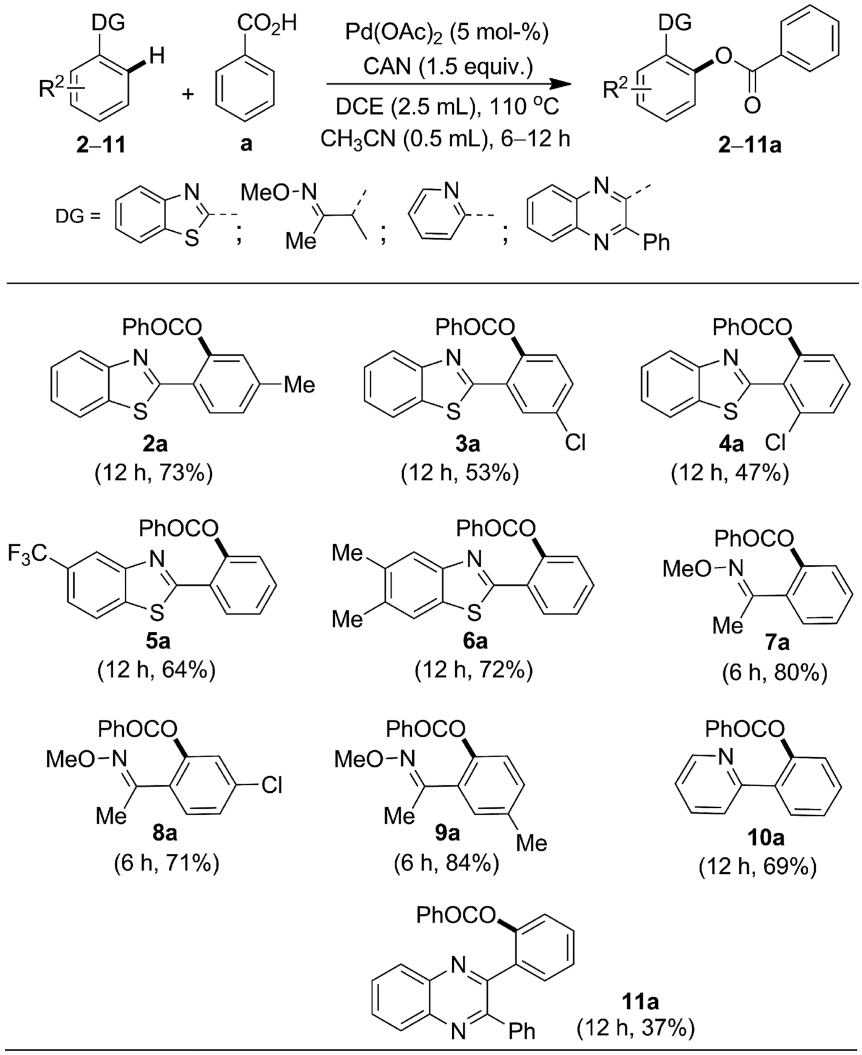
This strategy was also successful with 2-aryl-substituted benzothiazoles that contained the electron-donating substituent *p*-Me (i.e., **2**) and moderately electron-withdrawing groups *m*-Cl and *o*-Cl (i.e., **3** and **4**). These substituted substrates provided the expected *o*-benzoxylated products **2a**, **3a**, and **4a**, respectively, as shown in Scheme 2. Substituted benzothiazoles that contained the electron-withdrawing –CF_3 group and electron-donating –Me group (i.e., **5** and **6**, respectively) gave *o*-benzoxylated products **5a** and **6a** in good yields (see Scheme 2). The versatility of CAN as an oxidizing agent was successfully demonstrated with other well-investigated directing arenes such as acetophenone *O*-methyl oxime, 2-phenylpyridine, and 2,3-diphenylquinoxaline. Under the present optimized conditions, acetophenone *O*-methyl oxime (**7**) provided the desired *o*-benzoxylated product **7a** in good yield (80%) in a shorter reaction time (6 h). Acetophenone *O*-methyl oxime that contained the electron-deficient *p*-Cl substituent (i.e., **8**) afforded a lower yield (71%) of *o*-benzoxylated product **8a**, whereas electron-rich *m*-methylacetophenone *O*-methyl oxime (**9**) gave the regioselective *o*-benzoxylated product **9a** in 84% yield. The most employed directing ligand moiety, 2-phenyl pyr-



Scheme 1. Scope of acids for *o*-benzoxylation of **1**.[a,b] [a] Reagents and conditions: **1** (0.5 mmol), carboxylic acid (0.6 mmol), and CAN (0.75 mmol) at 110 °C for 12 h. [b] Isolated yield. [c] The remainder was unreacted starting materials.

idine (**10**), provided *o*-benzoxylated product **10a** in 69% yield by using CAN. This yield is comparable with those reported by other groups that employed Pd^{II}/CuI/Ag_2CO_3[2c] and $Rh^{I}/P(Cy)_3{\cdot}HBF_4$/CuI[2e] combinations and is slightly lower than that obtained by using the Pd^{II}/PhI-$(OCOR)_2$[1a] catalytic system. However, the 2,3-diphenylquinoxaline (**11**) directing system afforded *o*-benzoxylated product **11a** in a mere yield of 37% (see Scheme 2).

Palladium-catalyzed decarboxylative cross-coupling reactions of benzoic acids are best carried out in the presence of silver or copper salts.[7] On the other hand, directed[8] or nondirected[9] decarboxylative cross-coupling reactions of α-keto acids are effective in the presence of either silver, a persulfate ($S_2O_8^{2-}$) source, or combination thereof, which makes the process economically unviable for large scale synthesis. Thus, we questioned whether CAN could act as an alternative for the silver salts, the persulfate ($S_2O_8^{2-}$), or combination thereof during a decarboxylative *o*-aroylation. To check the efficacy of CAN as a terminal oxidant, a CDC reaction between 2-phenylbenzothiazole (**1**, 1 equiv.) and phenylglyoxylic acid (**a′**) (1.2 equiv.) was carried out in the presence of $Pd(OAc)_2$ (5 mol-%) and CAN (1.5 equiv.) in 1,2-dichloroethane. The desired *o*-aroylated product **1a′** was obtained in a paltry yield of 26%. With this preliminary success, to achieve the best possible conversion, other reaction parameters such as solvent, catalyst, oxidant, and their quantities were varied (see Table 2). Other oxidants were also examined for comparison. The optimization results indicate that the decarboxylative coupling between 2-phenylbenzothiazole (**1**, 1 equiv.) and phenylglyoxylic acid (**a′**,



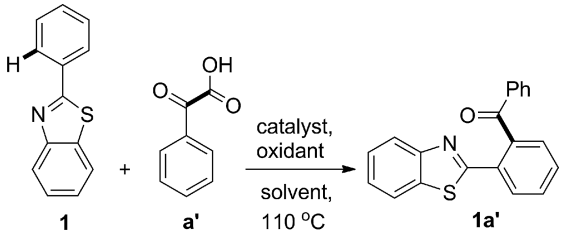
Scheme 2. Scope of directing groups for *o*-benzoxylation.[a,b] [a] Reagents and conditions: directing arene (0.5 mmol), benzoic acid (0.6 mmol), and CAN (0.75 mmol) at 110 °C for 6–12 h. [b] Isolated yield.

1.2 equiv.) was best achieved by using $Pd(OAc)_2$ (10 mol-%) and CAN (1.5 equiv.) in DMF at 110 °C (see Table 2). These standardized conditions were used to examine the decarboxylative *o*-aroylation reactions of a range of directing arenes.

Direct *o*-aroylation reactions have primarily been accomplished by using three different approaches. In substrate-directed CDC approaches, aldehydes[6a,10] and benzyl alcohols[11] are employed as aroyl surrogates. By using alkylbenzenes as the synthetic equivalent of the aroyl moiety, our group and others have recently demonstrated their installation at the *ortho* site of various directing substrates.[12] However, the most striking *o*-aroylation strategy is through the decarboxylation of α-ketocarboxylic acids. Thus, using above standardized conditions, we scrutinized the scope and generality of a decarboxylative coupling reaction with various 2-aryl-substituted benzothiazoles and phenylglyoxylic acid (**a′**). 2-Phenylbenzothiazole that contained electroneutral –H (i.e., **1**), electron-donating *p*-Me, *p*-OMe, and *p*-*t*Bu (i.e., **2**, **12**, and **13**), and electron-withdrawing *o*-Cl , *m*-Br, and *p*-Cl (i.e., **4**, **14**, and **15**) substituents on the 2-phenyl ring coupled efficiently with **a′** to provide the desired *o*-aroylated products in moderate to good yields (see Scheme 3). However, no correlation could be ascertained between the effect of substituent on the 2-phenyl ring of the 2-arylbenzothiazole and the yield of product. *m*-Bromo-substituted 2-arylbenzothiazole **14** provided *o*-aroylated product **14a′** with the reaction occurring at the less sterically hindered *ortho* site as a result of a favorable cyclopalladation step. The presence of the strong electron-withdrawing $–CF_3$ substituent on the benzothiazole ring of **5** provided a comparable yield of **5a′** to that of electroneutral substrate **1** (see Scheme 3).

2-Phenylbenzoxazole (**16**), a structural analogue of 2-phenylbenzothiazole (**1**), provided *o*-aroylated product **16a′** in low yield (44%), even by using an excess amount of $Pd(OAc)_2$ (15 mol-%) and after a prolonged reaction time (48 h). Similarly, *p*-Me-substituted 2-phenylbenzoxazole **17** gave a meager yield of 40% under the identical conditions. However, for substrate **16**, well-established oxidants[8] such

Table 2. Screening of reaction conditions for *o*-aroylation.



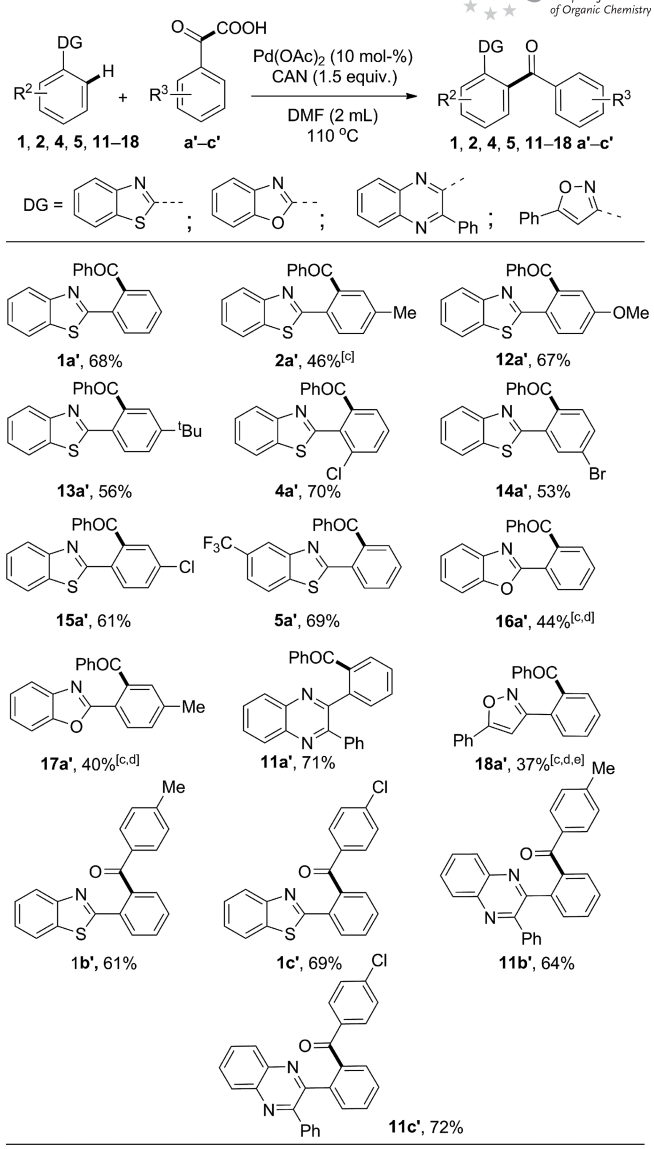
1 a' 1a'

Entry	Catalyst [mol-%]	Solvent	Oxidant	Yield [%][a,b]
1	$Pd(OAc)_2$ (5.0)	DCE	CAN	26
2	$Pd(OAc)_2$ (5.0)	cyclohexane	CAN	8
3	$Pd(OAc)_2$ (5.0)	dioxane	CAN	34
4	$Pd(OAc)_2$ (5.0)	toluene	CAN	39
5	$Pd(OAc)_2$ (5.0)	DMF	CAN	47
6	$Pd(OAc)_2$ (5.0)	DMSO	CAN	0[c]
7	$Pd(OAc)_2$ (10.0)	DMF	CAN	68
8	$Pd(OAc)_2$ (2.0)	DMF	CAN	32
9	$Pd(TFA)_2$[d] (10.0)	DMF	CAN	44
10	$PdCl_2$ (10.0)	DMF	CAN	53
11	$PdBr_2$ (10.0)	DMF	CAN	35
12	$Pd(OAc)_2$ (10.0)	DMF	Ag_2CO_3	0[c]
13	$Pd(OAc)_2$ (10.0)	DMF	$K_2S_2O_8$	60
14	$Pd(OAc)_2$ (10.0)	DMF	$(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$	41

[a] Reagents and conditions: 2-arylbenzothiazole (0.25 mmol), phenylglyoxylic acid (0.30 mmol), and oxidant (0.38 mmol) at 110 °C for 8 h. [b] Isolated yield. [c] Complete recovery of starting materials. [d] Palladium(II) trifluoroacetate is $Pd(TFA)_2$.

as Ag^I failed to give the desired product, whereas the use of persulfate ($S_2O_8^{2-}$) gave a comparable yield to that by using CAN.

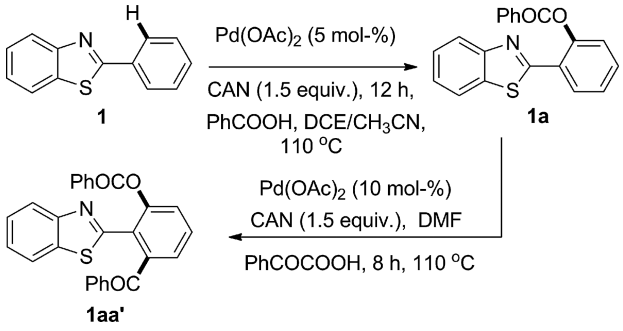
The usefulness of CAN as an oxidizing agent was then successfully applied to directing arene 3,5-diphenylisoxazole (**18**). 3,5-Diphenylisoxazole (**18**) with *N* and *O*-chelating atoms provided the expected *o*-aroylated product **18a′** but in a lower yield (37%). The product yields for these oxygen-containing *N*-directed substrates **16**, **17**, and **18** are less than those of the sulfur-containing ones (see Scheme 3). Because of its oxophilic nature, the cerium atom possibly remains bound to the oxygen atom of the oxygen-containing directing arene, thereby making it unavailable for the oxidative addition and giving lower yields. However, the directing arene that contains two nitrogen atoms, as in the case of 2,3-diphenylquinoxaline (**11**), provided *o*-aroylated product **11a′** in good yield (71%) under the optimized reaction conditions. It is worth noting that none of the above-mentioned directing groups have been previously employed in a decarboxylative *o*-aroylation reaction with phenylglyoxylic acid. Further *o*-aroylations of directing arenes **1** and **11** were carried out with substituted phenylglyoxylic acids. *p*-Methyl-substituted phenylglyoxylic acid **b′** coupled efficiently with both directing arenes **1** and **11** to provide their desired products **1b′** and **11b′** in almost identical yields (see Scheme 3). The coupling reaction of *p*-Cl-substituted phenylglyoxylic acid **c′** with **1** and **11** proceeded better than those of *p*-Me-substituted phenylglyoxylic acid **b′** and provided *o*-aroylated products **1c′** and **11c′**.



Scheme 3. Substrate scope for decarboxylative *o*-aroylation[a,b] [a] Reagents and conditions: directing arene (0.25 mmol), α-keto acid (0.30 mmol), and CAN (0.38 mmol) at 110 °C for 8 h. [b] Isolated yield. [c] The remainder was recovered starting materials. [d] Reactions were performed for 48 h by using 15 mol-% $Pd(OAc)_2$. [e] DCE was used in lieu of DMF.

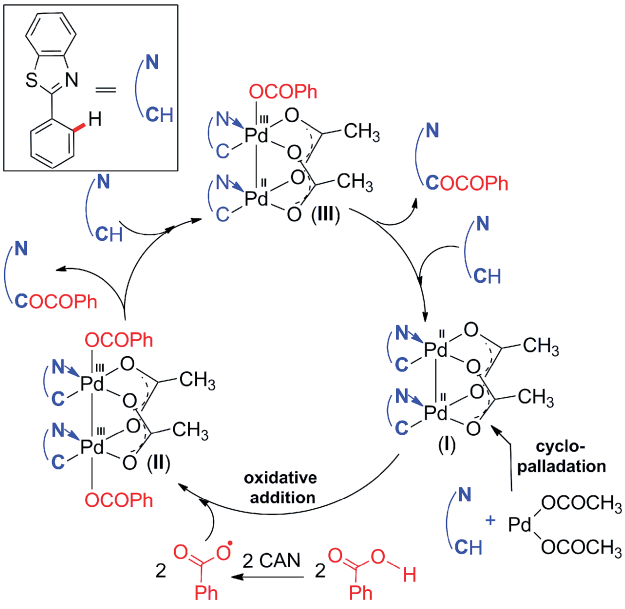
To demonstrate the synthetic utility of CAN as a terminal oxidant, both *o*-benzoxylation and *o*-aroylation strategies were successfully applied in sequence (as a one-pot reaction) for the construction of the *o*-bifunctionalized compound 2-(benzo[*d*]thiazol-2-yl)-3-benzoylphenyl benzoate (**1aa′** see Scheme 4). For this, 2-phenylbenzothiazole (**1**) was chosen as the directing arene, and product **1aa′** was obtained in 30% overall yield.

Taking cues from the above experimental observations, plausible mechanisms can be proposed for both the *o*-benzoxylation and *o*-aroylation reactions (see Scheme 5). When a typical *o*-benzoxylation or *o*-aroylation was carried out in the presence of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 1 equiv.), significant reductions in the product yields (5–7%) were observed,



Scheme 4. One-pot heterobifunctionalization of 2-phenylbenzothiazole (**1**).

thereby supporting a radical pathway for these processes. Because of the formation of relatively stable benzoxy radicals from aromatic acids that have an electron-withdrawing group, these substrates afforded better yields of product than those obtained by using aromatic acids that have electron-donating groups. When the benzoxylation of **1** was carried out in the presence of 1, 1.5, and 2 equiv. of oxidant (CAN) under otherwise identical conditions, the isolated yields of the product after 12 h were 66, 71, and 72% respectively. These experiments suggest a minimum requirement of 1 equiv. of oxidant is needed for this transformation, thereby indicating a Pd^{II}/Pd^{III} catalytic cycle.[13]



Scheme 5. Proposed mechanism for *o*-benzoxylation.

For the *o*-benzoxylation process, the initial cyclopalladation of 2-phenylbenzothiazole (**1**) leads to the formation of acetate bridged binuclear Pd^{II} intermediate **I** (see Scheme 5). This dimeric Pd^{II} complex further undergoes a bimetallic oxidative addition with the in situ generated benzoxy radical that is obtained by the action of CAN with benzoic acid. The proximity of the two Pd centers might facilitate cooperative redox chemistry, in which both metals participate synergistically to lower the barrier of the redox transformation. The oxidative addition product is dimeric Pd^{III}[13] intermediate **II**, as was detected by mass spectral analysis of the reaction mixture (see Supporting Information, Figure S1). Furthermore, the detection of a monomeric Pd^{IV}[14] species in the reaction aliquot[15] (see Supporting Information, Figure S1) may be the result of a Pd–Pd cleavage in dimeric Pd^{III} intermediate **II** to give monomeric Pd^{IV}[14d] and Pd^{II} species. A reductive elimination leads to the *o*-benzoxylated product and forms the active dimeric species **III**. Intermediate **III** further releases another *o*-benzoxylated product by C–O bond formation and regenerates dinuclear Pd^{II} active species **II** for the next catalytic cycle. For the decarboxylative *o*-aroylation process, the detection of TEMPO ester (**E**) along with quenching the reaction supports the formation of an aroyl radical (see Supporting Information). A similar mechanism could be envisaged for the *o*-aroylation process.

Conclusions

In summary, we have demonstrated the use of the inexpensive terminal oxidant CAN as an efficient substitute for a set of expensive oxidants/additives in the Pd-catalyzed substrate-directed *o*-benzoxylation and decarboxylative *o*-aroylation processes that proceed through a CDC reaction. Mechanistic investigations reveal a radical pathway for both of these strategies.

Experimental Section

Synthesis of 2-(Benzo[*d*]thiazol-2-yl)phenyl Benzoate (1a) from 2-Phenylbenzothiazole (1) and Benzoic Acid (a): To an oven-dried round-bottomed flask (25 mL) fitted with a reflux condenser were added 2-phenylbenzothiazole (**1**, 0.105 g, 0.5 mmol), benzoic acid (0.073 g, 0.6 mmol), $Pd(OAc)_2$ (0.006 g, 0.025 mmol), ceric ammonium nitrate (0.411 g, 0.75 mmol), 1,2-dichloroethane (2.5 mL), and acetonitrile (0.5 mL). The reaction mixture was heated at reflux in an oil bath that was preheated to 110 °C. Upon completion of the reaction (12 h), the solvent was evaporated under reduced pressure, and the reaction mixture was combined with ethyl acetate (30 mL). The ethyl acetate layer was carefully washed with saturated sodium hydrogen carbonate solution (2 × 5 mL), dried with anhydrous sodium sulfate, and evaporated under reduced pressure. The crude product was purified over a silica gel column (hexane/ethyl acetate, 10:0.2) to give pure 2-(benzo[*d*]thiazol-2-yl)phenyl benzoate (**1a**, 0.117 g, 71% yield). The identity and purity of the product was confirmed by spectroscopic analysis.

Synthesis of (2-Benzothiazol-2-ylphenyl)-phenyl-methanone (1a′) from 2-Phenylbenzothiazole (1) and Phenylglyoxylic Acid (a′): An oven-dried flask was charged with 2-phenylbenzothiazole (**1**, 0.053 g, 0.25 mmol), phenylglyoxylic acid (**a′**, 0.045 g, 0.30 mmol), ceric ammonium nitrate (0.206 g, 0.38 mmol), and $Pd(OAc)_2$ (0.006 g, 0.025 mmol) in DMF (2 mL). The reaction mixture was then stirred in a preheated oil bath at 110 °C for 8 h. After the stipulated time, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (30 mL). The organic layer was subsequently washed with a saturated solution of sodium hydrogen carbonate solution (2 × 5 mL). The ethyl acetate layer was then dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by chromatography on a silica

gel column (hexane/ethyl acetate, 10:0.5) to yield the pure 2-(benzothiazol-2-ylphenyl)-phenyl-methanone (**1a′**, 0.054 g, yield 68%).

Supporting Information (see footnote on the first page of this article): General methods, details of crystal structure analysis of **1a**, mechanistic investigation, and spectra for all compounds.

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[16] CCDC-997276 (for **1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For additional details, see the Supporting Information.

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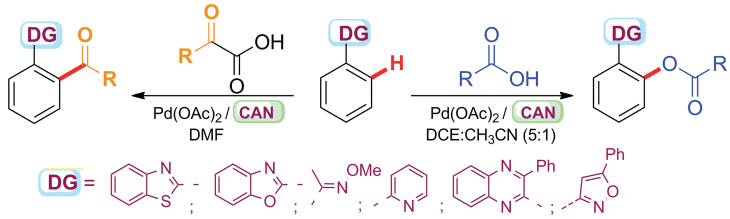
C–H Functionalization



CAN can activate: Inexpensive ceric ammonium nitrate (CAN) is an efficient oxidant for the Pd-catalyzed substrate-directed *o*-benzoxylation and decarboxylative *o*-aroylation processes. In the presence of CAN, the reaction of directing arenes with carboxylic acids resulted in *o*-benzoxylated products, and that with α-keto acids led to the formation of *o*-aroylation products.

Keywords: Synthetic methods / C–H activation / Cross-coupling / Oxidation / Palladium / Cerium / Regioselectivity

