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Rate Enhancement in CAN-Promoted $Pd(PPh_3)_2Cl_2$-Catalyzed Oxidative Cyclization: Synthesis of 2-Ketofuran-4-carboxylate Esters

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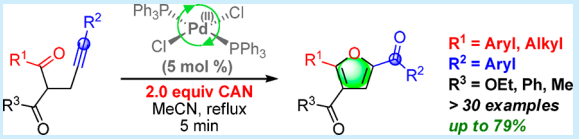
Supporting Information

ABSTRACT: Stoichiometric ceric ammonium nitrate (CAN) and a catalytic amount of $Pd(PPh_3)_2Cl_2$ (5 mol %) can rapidly produce multisubstituted 2-ketofuran-4-carboxylate esters from 2-propargylic 1,3-ketoesters via oxidative *O*-cyclization reaction. $Pd(PPh_3)_2Cl_2$ was found to be the crucial catalyst as its inclusion greatly enhanced the rate of the reaction and cleanly afforded the products within minutes. Over 30 substrates were successfully converted to the desired compounds in mostly moderate to good yields.



Ceric ammonium nitrate (CAN) has been frequently employed as a single-electron oxidant[1] in various oxidative transformations of organic compounds[2] because it is comparatively affordable, stable, and convenient to handle. CAN has been employed in synthesis of various carbocyclic and heterocyclic compounds, and the utilization of CAN in organic transformations has been extensively reviewed.[3] We intended to study and utilize CAN in an *O*-cyclization reaction for the construction of multisubstituted 2,4-diacylfurans.

2,4-Diacylfurans are substructures widely found in several natural compounds significantly relevant to human health. An analogue of urofuranoic acid, CMPF[4] (Figure 1), has recently

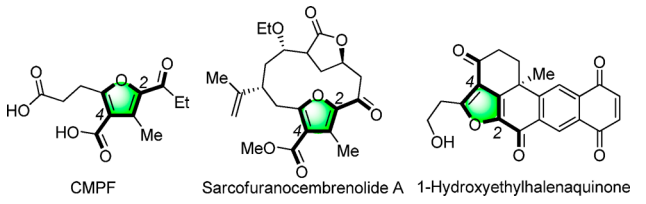
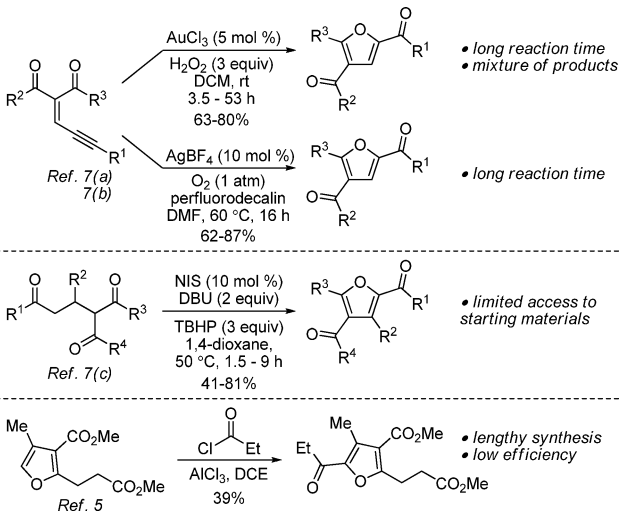


Figure 1. Examples of natural compounds containing 2,4-diacylfuran substructures.

been suspected to induce gestational diabetes (GD) in pregnant women and type 2 diabetes mellitus (T2DM) in mouse and human. The increase of CMPF in plasma shows a direct correlation with the decrease in glucose-induced secretion of insulin. It has also been linked to occurrence of chronic kidney disease (CKD).[4c] Several natural products of valuable medicinal properties containing 2,4-diacylfuran skeletons have also been discovered and biologically evaluated as exemplified in Figure 1.[5]

During a literature survey, we realized that only a few synthetic methods were known for the synthesis of this class of compounds. They usually required high reaction temperatures, long reaction times, and specific starting materials (Scheme 1).[6] Development of a new method to prepare this valuable

Scheme 1. Reported Syntheses of 2,4-Diacylfurans



core scaffold that overcomes these limitations is desirable. Herein, we reported an extremely rapid (within minutes), effective, and convenient conversion of 2-propargylic 1,3-ketoesters to trisubstituted 2-acyl-4-carboxylate furans.

We started by using ketoester **1a** to screen for optimal conditions. By employing only CAN in refluxing MeCN,

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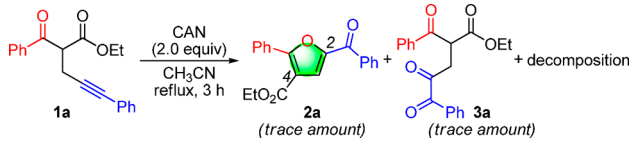
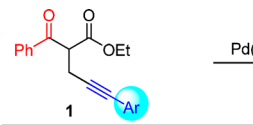
ketoester **1a** was sluggishly converted to only trace amounts of furan **2a** and side product **3a** in a complex mixture after 3 h (Scheme 2). We envisioned that transition metals may assist in

Scheme 2. CAN-Promoted Reactions of 1,3-Ketoester 1a



activating the substrate for this cyclization. Therefore, a number of transition metals were investigated as an additive in the reaction. Further optimization[7a] identified the most optimal conditions to require 5 mol % of $Pd(PPh_3)_2Cl_2$ and 2.0 equiv of CAN in refluxing MeCN. Under these conditions, ketoester **1a** was fully consumed within 5 min, and furan **2a** was obtained in 71% while compound **3a** was not observed at all. The efficiency of the reaction was not affected by moisture as observed during the optimization. However, the reaction seemed to require oxygen as lower yield of **2a** was observed when oxygen was excluded. The use of two or more transition metals in organic synthesis has been recognized as an effective tool for many organic reactions,[8] especially Pd(II) complexes which had been utilized with various metals.[9] For Ce(IV) species, there had been only two examples showing its utilization with other metals.[10] Specifically, only one example of Pd(II)−Ce(IV)-promoted reaction was reported,[10b] although the interactions of these two metal species had been studied in the context of redox chemistry.[11] The scope of this reaction was next studied as shown in Scheme 3.

Scheme 3. Oxidative Cyclization of 1 (Varying Ar Groups)[a]



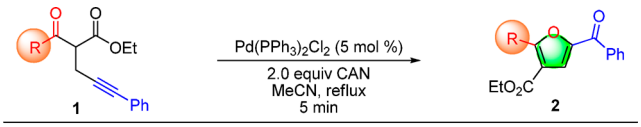
2-H;	Ar = H	*46%*
2a;	Ar = Ph	*71%*
2b;	Ar = 2-OMe-C_6H_4	*31%*
2c;	Ar = 3-OMe-C_6H_4	*61%*
2d;	Ar = 4-OMe-C_6H_4	*17%*
2e;	Ar = 4-F-C_6H_4	*59%*
2f;	Ar = 2-Cl-C_6H_4	*52%*
2g;	Ar = 3-Cl-C_6H_4	*54%*
2h;	Ar = 4-Cl-C_6H_4	*63%*
2i;	Ar = 4-CO_2Me-C_6H_4	*63%*
2j;	Ar = 4-CF_3-C_6H_4	*64%*
2k;	Ar = 4-CN-C_6H_4	*70%*
2l;	Ar = 4-NO_2-C_6H_4	*68%*
2m;	Ar = 2-NHAc-C_6H_4	*46%*

[a]Isolated yields.

In addition to internal alkyne **1a**, the conditions were applied to terminal alkyne substrate **1-H**, which produced furfural **2-H** in satisfactory yield (46%). The electronic properties of aryl alkynes were explored. Reaction of **1b** (Ar = 2-OMe-C_6H_4) gave **2b** in 31% yield, while **1c** (Ar = 3-OMe-C_6H_4) was converted to **2c** in significantly better yield (61%). However, the reaction of **1d** (Ar = 4-OMe-C_6H_4) gave 17% yield of **2d**. Side reactions involving reactive *o*-quinone and *p*-quinone methide-type intermediates were suspected for substrates **1b** and **1d**, while in compound **1c**, such an intermediate could not be formed, and therefore, a higher yield of **2c** was achieved. Furan **2b** was also obtained in higher yield (31%) than **2d** (17%). This was probably due to the steric hindrance of 2-OMe group making **1b** less likely to form *o*-quinone methide-type species than **1d**. This thus contributed to more side reactions of **1d** and a lower yield of **2d**. For fluoro- and chlorophenyl substrates (**1e−h**), the reactions produced furans **2e−h** in moderate yields (52−63%). For **1i−l**, containing strongly *p*-electron-withdrawing groups, the reactions led to furans **2i−l** in moderate yields (63−70%). These results demonstrated a strong trend that mildly electron-deficient substrates (**1e−h**) and strongly electron-deficient substrates (**1i−l**) produced furan products in better yields than electron-rich substrates, with the exception of substrate **1c** that the 3-OMe group acted more as electron-withdrawing group via inductive effect. Next, **1m** (Ar = 2-NHAc-C_6H_4) could be converted to furan **2m** in moderate yield (46%). The *N*-acetyl group helped reduce the electron-donating effect of the nitrogen, thus resulting in moderate yield of the product.

Variation of R groups was next studied (Scheme 4). Substrate **1n** (R = 2-OMe-C_6H_4) underwent the cyclization

Scheme 4. Oxidative Cyclization of 1 (Varying R Groups)[a]



2n;	R = 2-OMe-C_6H_4	*39%*
2o;	R = 3-OMe-C_6H_4	*65%*
2p;	R = 4-OMe-C_6H_4	*59%*
2q;	R = 3,4,5-$(OMe)_3$-C_6H_2	*21%*
2r;	R = 2-F-C_6H_4	*60%*
2s;	R = 4-F-C_6H_4	*79%*
2t;	R = 4-Br-C_6H_4	*62%*
2u;	R = 4-NO_2-C_6H_4	*44%*
2v;	R = 2-Me-C_6H_4	*36%*
2w;	R = 1-naphthyl	*28%*
2x;	R = 2-naphthyl	*67%*
2y;	R = 3-(*N*-Ts-indolyl)	*44%*
2z;	R = 2-benzothiophenyl	*45%*
2aa;	R = *n*-Pr	*35%*

[a]Isolated yields.

to give the desired product (**2n**) in 39% yield, which may have been caused by steric hindrance of the 2-OMe group during the C−O cyclization. Reaction of **1o** (R = 3-OMe-C_6H_4) proceeded to give **2o** in 65% yield, while a slightly lower yield (59%) of **2p** was obtained from ketoester **1p** (R = 4-OMe-C_6H_4). For these substrates, the methoxy groups did not impose steric hindrance in the reactions. However, reaction of **1q** (R = 3,4,5-$(OMe)_3$-C_6H_2) produced only 21% of **2q**. Multiple methoxy groups in the aryl ring may have made it highly probable to form reactive species under the conditions, thus leading to more side reactions and a lower yield of **2q**. In contrast, compounds **1r−t**, containing halogen substituents, reacted more smoothly to provide products **2r−t** in moderate to good yields. However, when R = 4-NO_2-C_6H_4 (**1u**), the reaction produced only 44% yield of furan **2u**. For more electronically neutral substrates, conversion of **1v** (R = 2-CH_3-C_6H_4) resulted in product **2v** in 36% yield. In this case, the steric hindrance of the 2-Me group imposed a negative impact to the yield similar to low yield observed in **2n**. Substrates bearing 1- and 2-naphthyl groups (**1w** and **1x**) were also attempted; the desired **2w** and **2x** were obtained in 28% and 67% yields, respectively. Similar to **1n** and **1v**, yield of **2w** was lower than that of **2x** due to the steric hindrance at the *ortho*-position present in the 1-naphthyl group. The reaction was also applicable to heteroaryl substrates as seen in the reactions of **1y** (R = 3-(*N*-Ts-indolyl)) and **1z** (R = 2-benzothiophenyl) in that products **2y** and **2z** were provided in 44% and 45% yields,

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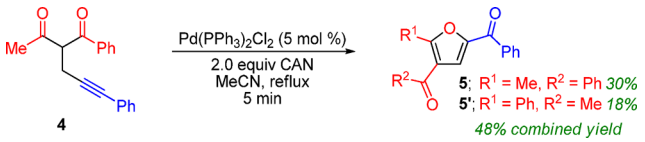
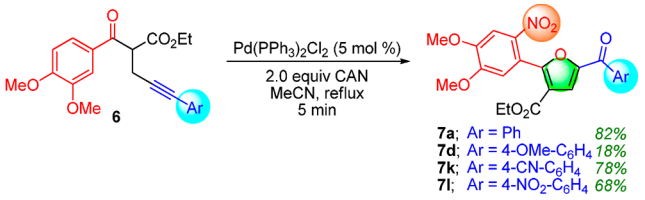
respectively. For alkyl ketoester, reaction of **1aa** (R = *n*-Pr) produced **2aa** in 35% yield. Furthermore, the reaction was performed with unsymmetrical 1,3-diketone **4**, which produced furan **5** (via acetyl oxygen cyclization) in 30% yield and furan **5′** (via benzoyl oxygen cyclization) in 18% yield. This result demonstrated the higher reactivity of alkyl ketone oxygen than the aryloyl oxygen (Scheme 5).

Scheme 5. Oxidative Cyclization of Unsymmetrical Dione 4



Surprisingly, substrates **6** (Scheme 6) underwent both oxidative cyclization and C-6 nitration[12] on the 3,4-

Scheme 6. Conversion of Substrates 6 to Products 7[a]



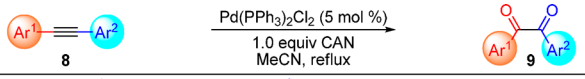
[a]Isolated yields.

dimethoxyaryloyl rings to produce furans **7**. A brief scope of this conversion was shown with substrates **6a**, **6d**, **6k**, and **6l**. The electronically neutral **6a** (Ar = Ph) gave **7a** in 82% yield,[7b] while the reaction of more electron-rich substrate **6d** (Ar = 4-OMe-C_6H_4) afforded **7d** in only 18% yield. For electron-deficient **6k** (Ar = 4-CN-C_6H_4) and **6l** (Ar = 4-NO_2-C_6H_4), the reactions provided furans **7k** and **7l** in 78%[7b] and 68% yields, respectively.

As revealed in Scheme 1, 1,2-diketone **3a** could also be detected as a side product from the reaction of **1a**. We decided to optimize this reaction into a more general protocol for converting diarylalkynes to 1,2-diaryldiketones with our bimetallic reagent system[13] by employing diphenylacetylene (**8a**) for screening. A brief optimization identified that 5 mol % of $Pd(PPh_3)_2Cl_2$ and 1.0 equiv of CAN were optimal, which led to diketone **9a** in 69% yield. The scope of the reaction was studied as shown in Scheme 7. When Ar^1 was a phenyl group (**8a**–**j**), products **9a**–**j** were generated mostly in moderate yields requiring different reaction times, with the exception of **9c**. In contrast, when Ar^2 was electron-deficient or inductively electron-deficient (**8b** and **8d**–**j**), products were obtained in moderate to good yields (55–76%). For substrates **8k**–**n**, the yield was highest for **9m** (62%).

As CAN was used in the reaction, a radical mechanism was suspected. Additional experiments were conducted with **1a** by including TEMPO and BHT as radical scavengers in the reaction. As shown in Table 1, although the reactions were not completely shut down in the presence of either reagent, possibly due to the more rapid intramolecular radical cyclization leading to the product, the presence of the radical scavenger did reduce the efficiency of the reaction in all cases. These results thus suggested the involvement of radical species. Rate enhancement of the reaction in the presence of 5 mol % of $Pd(PPh_3)_2Cl_2$ was studied with substrate **1l** using ^{1}H NMR

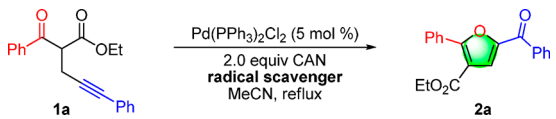
Scheme 7. Oxidation of Alkynes 8 to 1,2-Diketones 9[a]



9a;	Ar^1 = Ph	Ar^2 = Ph	3 h	69%
9b;	Ar^1 = Ph	Ar^2 = 3-OMe-C_6H_4	8 h	57%
9c;	Ar^1 = Ph	Ar^2 = 4-OMe-C_6H_4	5 h	26%
9d;	Ar^1 = Ph	Ar^2 = 4-F-C_6H_4	3 h	58%
9e;	Ar^1 = Ph	Ar^2 = 4-Cl-C_6H_4	2 h	62%
9f;	Ar^1 = Ph	Ar^2 = 4-Br-C_6H_4	6 h	59%
9g;	Ar^1 = Ph	Ar^2 = 4-CO_2Me-C_6H_4	3 h	56%
9h;	Ar^1 = Ph	Ar^2 = 4-CF_3-C_6H_4	24 h	76%[b]
9i;	Ar^1 = Ph	Ar^2 = 4-CN-C_6H_4	8 h	55%
9j;	Ar^1 = Ph	Ar^2 = 4-NO_2-C_6H_4	3 h	64%
9k;	Ar^1 = 4-OMe-C_6H_4	Ar^2 = 4-OMe-C_6H_4	1 h	33%
9l;	Ar^1 = 4-OMe-C_6H_4	Ar^2 = 4-NO_2-C_6H_4	3 h	35%
9m;	Ar^1 = 4-Cl-C_6H_4	Ar^2 = 4-NO_2-C_6H_4	5 h	62%
9n;	Ar^1 = 4-$NO_2C_6H_4$	Ar^2 = 4-NO_2-C_6H_4	2 h	36%[c,d]

[a]Isolated yields. [b]Reaction was conducted at room temperature. [c]2.0 equiv of CAN was required. [d]Reaction was incomplete, and 41% of **8n** was recovered.

Table 1. Experiments To Verify a Radical Process



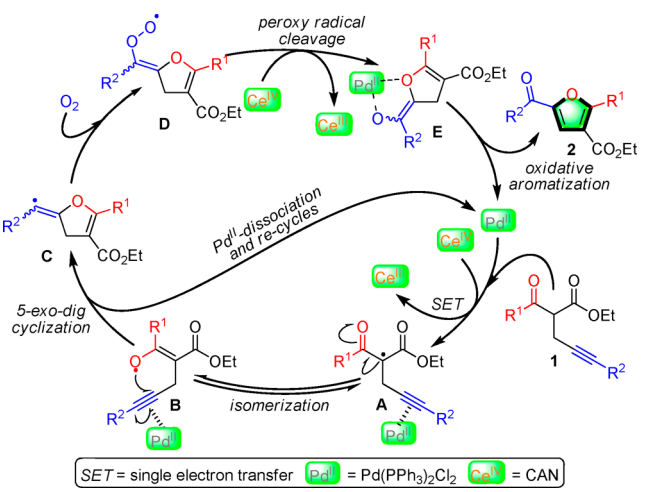
scavenger	equiv	time (min)	yield[a] (%)
TEMPO[b]	1.0	5	62
	2.0	15	53
BHT[c]	1.0	20	62[d]
	2.0	120	17

[a]Isolated yields unless noted. [b](2,2,6,6-Tetramethylpiperidin-1-yl)-oxyl. [c]Butylated hydroxytoluene. [d]Determined by ^{1}H NMR.

to monitor percent conversion versus time (see the Supporting Information). The results clearly showed that the Pd(II) catalyst could enhance the rate of conversion. The reaction cleanly went to completion (≥99%) within 6 min, whereas the reaction without the catalyst provided only 45% conversion with much inferior cleanliness in the same duration.

The mechanism of the oxidative cyclization of **1** was proposed as shown (Scheme 8). Ketoester **1** was oxidized via an SET process at the α-carbon to give radical **A**, which then isomerized to enolic oxygen-centered radical **B**. A rapid intramolecular cyclization of this radical promoted by Pd(II)

Scheme 8. Proposed Mechanism in the Oxidative Cyclization of Ketoesters 1 to Furans 2



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complex in 5-*exo*-*dig* fashion led to vinyl radical **C**. As the reaction optimization showed that the reaction was not sensitive to water, it was most likely that radical **C** combined with atmospheric oxygen to result in the formation of peroxy radical **D**. Cleavage of the peroxy radical by Ce(IV)[14] then ensued to produce dihydrofuran intermediate **E**, which then underwent oxidative aromatization to yield the desired furan **2**.

In summary, catalytic $Pd(PPh_3)_2Cl_2$ could immensely enhance the reactivity of CAN in the oxidative cyclization of 2-propargylic 1,3-ketoesters to furnish 2-ketofuran-4-carboxylate esters. A wide range of substrates were converted to furan products in mostly moderate to good yields within an extremely short reaction time (less than 5 min) under mild conditions. With a slight change of conditions, 1,2-diaryldiketones could be prepared via oxidation of diarylalkynes in moderate to good yields. Studies of the catalytic species as well as roles of Pd(II) species in the reaction are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00053.

Optimization, time−conversion studies, experimental procedures, spectroscopic data, and NMR spectra of compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(7) (a) For details, see the Supporting Information. (b) The reactions were carried out on larger than 1 mmol scales.

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