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Palladium-catalyzed direct carbonylation of thiophenes and furans under CO/CO$_2$-binary conditions leading to carboxylic acids††

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In this study, novel catalytic carbonylation of thiophenes and furans was successfully achieved by using a catalytic amount of Pd(OAc)$_2$ (min. 1 mol%). The catalyst showed excellent catalytic performance under CO/CO$_2$-binary conditions, and the use of *p*-benzoquinone (*p*-BQ) as a stoichiometric oxidant for the regeneration of high-valent palladium catalysts active for C–H bond activation of heteroaromatics successfully led to the corresponding carboxylic acids in up to quantitative yields. Conventional palladium-promoted direct carbonylation of heteroaromatics was difficult to conduct as a catalytic reaction due to the thermal decomposition of palladium active species. In sharp contrast, we found for the first time that the thermal decomposition of the catalyst could be suppressed by using a CO/CO$_2$-binary system; thus, highly efficient conversion of thiophenes and furans to the corresponding carboxylic acids has been attained with only 1 mol% catalyst loading. In the catalytic reactions, CO is the carbonyl source. The control experiments clearly showed that pressurized CO$_2$ suppresses the thermal decomposition of the active palladium species to inactive palladium black and improves the durability of the catalyst under reaction conditions. The direct and catalytic carbonylation *via* C–H bond activation has been considered one of the most challenging reactions; therefore, the method established in this study will lead to a novel, practical, and versatile transformation based on direct carbonylation.

Introduction

Functional heterocycles, which are the basis for pharmaceuticals and light-emitting materials, have attracted much attention because of their excellent properties as functional molecules. However, rapid and straightforward methods for introducing functional groups into heterocycles, which are the starting point for materials synthesis, have not yet been fully established. Therefore, many problems remain for multi-step molecular transformation and the disposal of large quantities of by-products and waste. Based on the background, the direct catalytic functionalization of heterocycles using transition-metal catalysts has been energetically investigated in recent decades.[1]

Among the transition-metal-catalyzed transformations, catalytic carbonylation has emerged as one of the key fundamental reactions in industrial and pharmaceutical fields. Thus, the development of highly efficient and green carbonylation has been strongly demanded using abundant CO as a C1 source.[2,3] Although there are many studies on transition-metal-catalyzed carbonylation, most of them have required the substrates pre-functionalized by halogen groups, directing groups, *etc.*, limiting the scope and applications.[4] From the background, direct carbonylation by C–H bond activation has attracted much attention in recent years.[5,6] However, the development of direct/catalytic carbonylation of aromatic compounds is almost unprecedented. In the 1990s, pioneering studies for palladium-promoted direct carbonylation of aromatics were reported; in the systems, an

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‡ This work is dedicated to Prof. Dennis P. Curran (University of Pittsburgh) on the occasion of his 70th birthday.
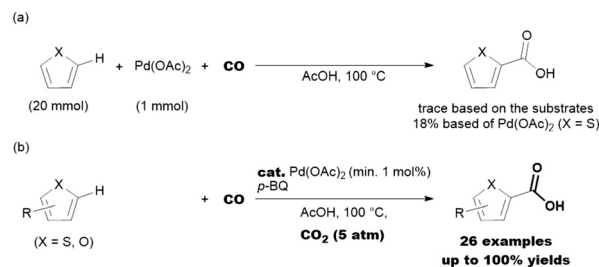
Scheme 1 (a) Precedent work for Pd-promoted carbonylation of thiophene/furan. (b) Pd-catalyzed direct carbonylation of thiophenes/furans (this work).

excess amount of furan or thiophene was required under CO, resulting in the corresponding carboxylic acids in trace yields (Scheme 1a).[7,8] Even today, direct, practical, and catalytic carbonylation of aromatics *via* C–H bond activation still remains as one of the unsolved problems in organic synthesis, and is now urgently needed for multi-functionalization directed to synthesis of functional molecules.

Herein, we report novel and direct catalytic oxidative carbonylation of thiophenes and furans using $Pd(OAc)_2$ as the catalyst, which exhibited excellent catalytic ability (min. 1 mol%) under a CO/CO_2-binary system to afford the corresponding carboxylic acids in up to quantitative yields (Scheme 1b).

Results and discussion

Initially, the carbonylation of 2-ethylthiophene **1a** (3 mmol) was investigated with $Pd(OAc)_2$ as the catalyst under CO (Table 1). The use of $Pd(OAc)_2$ (10 mol%) under CO (20 atm) afforded the corresponding carboxylic acid **2a** in 9% yield (entry 1). Interestingly, the yield of **2a** was slightly improved under CO (20 atm)/CO_2 (1 atm) (entry 2). Addition of *p*-benzoquinone (*p*-BQ) as the stoichiometric oxidant was effective for the regeneration of the reactive palladium species for C–H bond activation, and increasing the amount of *p*-BQ successfully improved the conversion of **1a**. As a result, **2a** was obtained in 75% yield with 3.0 equiv. of *p*-BQ under CO/CO_2 (entries 3 and 4). Comparing the oxidant, *p*-BQ was the most effective (entries 3–6). Further increasing the CO pressure to 50 atm somewhat improved the yield of **2a** (entry 7). Interestingly, the conversion of **1a** to **2a** was dramatically improved by pressurizing CO_2 to 5 atm (entry 8). Based on the result, further optimization was conducted under pressurized CO_2. Finally, **2a** was successfully obtained quantitatively by using $Pd(OAc)_2$ (1 mol%) and *p*-BQ (1.5 equiv.) under CO (30 atm)/CO_2 (5 atm) at 100 °C (entry 9). This catalytic carbonylation could be conducted even under

CO (10 atm)/CO_2 (5 atm) with $Pd(OAc)_2$ (3 mol%) with excellent conversion of **1a** to **2a** (entry 10). Decreasing the reaction temperature to 70 °C afforded **2a** in 67% yield (entry 11). Control experiments showed that both CO and CO_2 were necessary for excellent conversion of **1a** to **2a** (entries 12 and 13). The control experiments clearly showed that CO was the carbonyl source, and CO_2 could assist the catalytic transformation (mechanistic details are discussed later).

Under the optimal conditions (entry 9, Table 1), the scope of the Pd-catalyzed carbonylation of thiophenes was investigated (Table 2). A variety of thiophenes with ethyl, methyl, *n*-pentyl, 2-ethylhexyl, benzyl, $BnOCH_2–$, phenyl, chloro, and bromo groups at the 2-positions were successfully transformed into the corresponding carboxylic acids in up to quantitative yields (**2a**–**2i**). Thiophene **1j** was tolerable, and **2j** was selectively obtained in 72% yield. Although the transformation of 1-benzothiophene did not proceed at all, the more electron-rich heterocyclic compound thieno[3,2-*b*]thiophene **1k** successfully afforded the corresponding carboxylic acid **2k** in 56% yield. For 3-substituted thiophenes, the corresponding carboxylic acids were obtained with good product selectivity and regioselectivity (**2l**–**2p**). It was noteworthy that the direct carbonylation could be conducted in gram-scale, and 10 mmol of **1a** successfully converted to **2a** in quantitative yield.
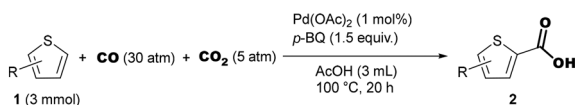
Among five-membered heterocycles, furans as well as thiophenes are one of the most important scaffolds for constructing functional materials. However, because furans are relatively unstable to heating, their reaction conditions are more restricted than those of thiophenes. Therefore, the construction of an efficient catalytic transformation has been required for the catalytic carbonylation of furans. In this study, the optimization of the reaction conditions for furans was also investigated in detail, and a variety of furans were successfully transformed into the corresponding carboxylic acids with excellent yields, as shown in Table 3 (see the ESI†). When furfuryl acetate **3a** was used as the substrate, using 5 mol% of

Table 1 Optimization of reaction conditions for Pd-catalyzed carbonylation of 2-ethylthiophene **1a**[a]
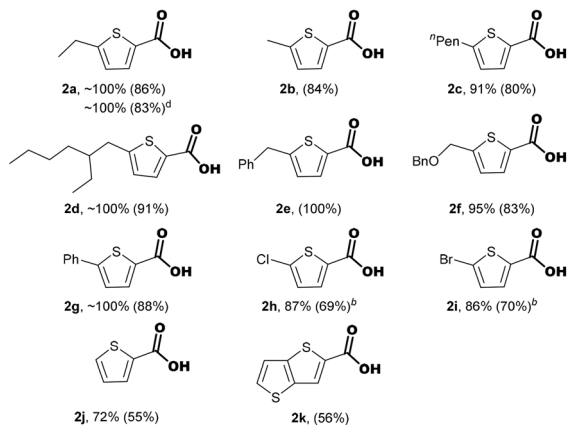

Entry	CO (atm)	CO_2 (atm)	$Pd(OAc)_2$ (mol%)	Additive (equiv.)	Yield of **2a** (%)
1	20	—	10	—	9
2	20	1	10	—	12
3	20	1	10	*p*-BQ (1.5)	61
4	20	1	10	*p*-BQ (3.0)	75
5	20	1	10	Chloranil (3.0)	Trace
6	20	1	10	Anthraquinone (3.0)	10
7	50	1	10	*p*-BQ (3.0)	83
8	50	5	10	*p*-BQ (3.0)	92
9	**30**	**5**	**1**	***p*-BQ (1.5)**	**~100 (86)**
10	10	5	3	*p*-BQ (1.5)	96
11[b]	30	5	1	*p*-BQ (1.5)	67
12	30	—	1	*p*-BQ (1.5)	72
13	—	5	1	*p*-BQ (1.5)	N. D.

[a] Yields were determined by ¹H NMR spectroscopy (isolated yield). [b] Reaction temperature: 70 °C.

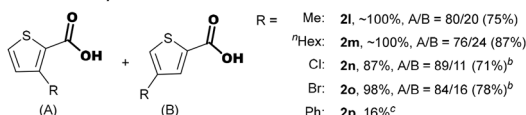This journal is © The Royal Society of Chemistry 2023

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Table 2 Reaction scope of Pd-catalyzed carbonylation of thiophenes[a]

For 2-substituted thiophenes:

2a, ~100% (86%) ~100% (83%)[d]

2b, (84%)

2c, 91% (80%)

2d, ~100% (91%)

2e, (100%)

2f, 95% (83%)

2g, ~100% (88%)

2h, 87% (69%)[b]

2i, 86% (70%)[b]

2j, 72% (55%)

2k, (56%)

For 3-substituted thiophenes:

R =	Me:	**2l**, ~100%, A/B = 80/20 (75%)
	nHex:	**2m**, ~100%, A/B = 76/24 (87%)
	Cl:	**2n**, 87%, A/B = 89/11 (71%)[b]
	Br:	**2o**, 98%, A/B = 84/16 (78%)[b]
	Ph:	**2p**, 16%[c]

[a] Yields were determined by ^{1}H NMR spectroscopy (isolated yields). [b] Pd(OAc)$_2$ (5 mol%) was used. [c] Isomer **B** was obtained selectively. [d] 2-Ethylthiophene **1a** (10 mmol) was used.

Table 3 Reaction scope of Pd-catalyzed carbonylation of furans[a]

4a, 92%[b]

4b, (78%)[c]

4c, (83%)[c]

4d, (79%)[c]

4e, 36%[c]

4f, (36%)[c]

4g, (82%)[b]

4h, (87%)[c]

4i, 61% (60%)[c,d]

4j, (95%)[c]

[a] Yields were determined by ^{1}H NMR spectroscopy (isolated yield). [b] Reaction conditions: Pd(OAc)$_2$ (5 mol%), 20 h. [c] Reaction conditions: Pd(OAc)$_2$ (15 mol%), 48 h. [d] Reaction temperature: 70 °C.
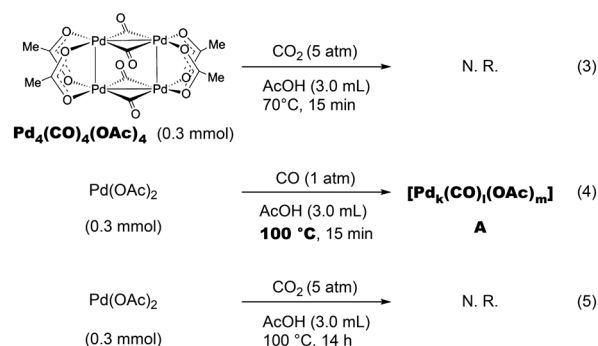
the Pd catalyst and 3.0 equiv. of *p*-BQ was effective to yield **4a** in 92% yield under CO (30 atm)/CO$_2$ (5 atm). It was noteworthy that 2-ethylfuran **3b**, which has no directing group such as the AcO group of **3a**, could be transformed into the corresponding carboxylic acid **4b** in 78% isolated yield by increasing the loading of Pd(OAc)$_2$ to 15 mol% and prolonging the reaction time to 48 h. Under the optimized conditions for direct carbonylation of furans, a variety of furans with *n*-propyl, *n*-butyl, methyl, phenyl, BnOCH$_2$–, and bromo groups at the 2-positions were successfully transformed into the corresponding carboxylic acids in moderate to good yields, respectively (**4c–4h**). For the transformation of furan **3i**, heating at 70 °C for 48 h using Pd(OAc)$_2$ (15 mol%) and *p*-BQ (3.0 equiv.) successfully afforded **4i** in 61% yield. Interestingly, when 3-bromofuran **3j** was used as the substrate, **4j** was regioselectively obtained as the sole product in 95% yield.[9]

To gain insights into the reaction pathways, some mechanistic experiments were conducted. When Pd(OAc)$_2$ (0.3 mmol) was heated under a CO atmosphere in AcOH (3.0 mL) at 50 °C for 15 min, a tetranuclear complex Pd$_4$(CO)$_4$(OAc)$_4$ was formed. Pd$_4$(CO)$_4$(OAc)$_4$ is a known compound, and the structure of the complex obtained by the reaction shown in eqn (1) was unambiguously determined by comparing its IR spectrum with that of the literature data (ν_{CO} = 1943 and 1972 cm^{-1}, eqn (1) in Fig. 1).[10] Interestingly, when Pd$_4$(CO)$_4$(OAc)$_4$ (*in situ* generated) was heated at 100 °C

for 15 min in AcOH under a CO$_2$ atmosphere, new absorption bands attributed to the CO vibration (ν_{CO} = 1946, 1958 cm^{-1}) were confirmed along with the acetate group vibration (ν = 1400–1600 cm^{-1}) by IR spectroscopy, indicating the formation of a novel Pd–CO complex Pd$_k$(CO)$_l$(OAc)$_m$ **A** (eqn (2) in Fig. 1). Since complex **A** was quite unstable, it was difficult to determine the structure of complex **A** by single crystal X-ray analysis, elemental analysis, and HRMS measurement.[11]

Heating the solution of Pd$_4$(CO)$_4$(OAc)$_4$ in AcOH at 70 °C for 15 min under CO$_2$ (5 atm) did not cause any transformation; thus, heating at 100 °C was necessary for the transformation of Pd$_4$(CO)$_4$(OAc)$_4$ into complex **A** (eqn (3)). Furthermore, complex **A** was also obtained directly by heating the solution of Pd(OAc)$_2$ in AcOH at 100 °C for 15 min under a CO atmosphere (1 atm) (eqn (4)). Besides, Pd$_4$(CO)$_4$(OAc)$_4$ or complex **A** was not formed from Pd(OAc)$_2$ under CO$_2$ (5 atm) in the absence of CO even heating at 100 °C for 14 h (eqn (5)).

Pd$_4$(CO)$_4$(OAc)$_4$ (0.3 mmol) → CO$_2$ (5 atm), AcOH (3.0 mL), 70 °C, 15 min → N. R. (3)

Pd(OAc)$_2$ (0.3 mmol) → CO (1 atm), AcOH (3.0 mL), **100 °C**, 15 min → [Pd$_k$(CO)$_l$(OAc)$_m$] **A** (4)

Pd(OAc)$_2$ (0.3 mmol) → CO$_2$ (5 atm), AcOH (3.0 mL), 100 °C, 14 h → N. R. (5)

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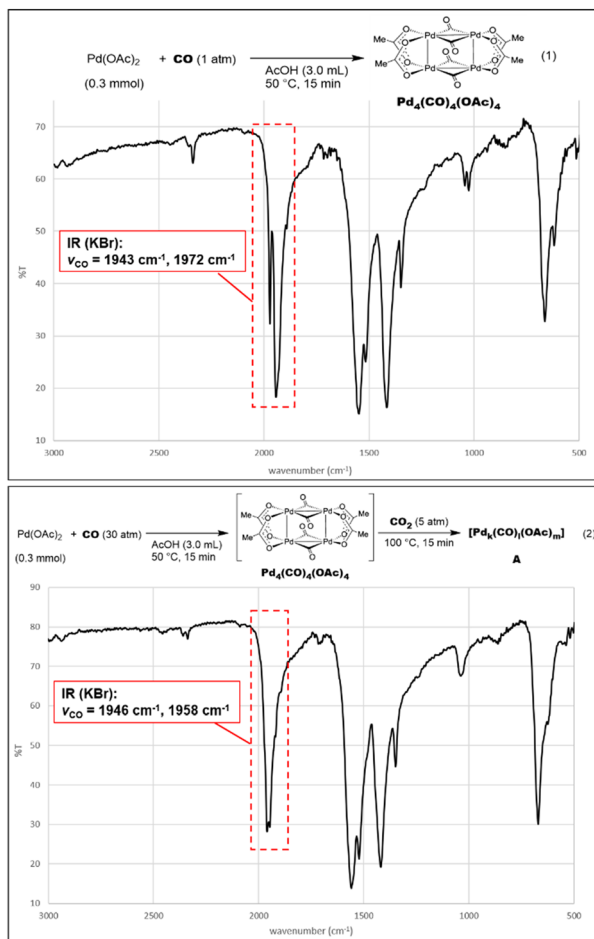This journal is © The Royal Society of Chemistry 2023

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Fig. 1 IR spectra of the solids obtained from the reactions of Pd(OAc)$_2$ with CO in AcOH.

These insights motivated us to investigate the catalytic performance of **A** (*in situ* generated) in catalytic carbonylation in the presence/absence of CO and CO$_2$ (Table 4). When the reaction was conducted under CO (30 atm), **2a** was obtained in 66% yield (entry 1). On the other hand, the reaction under CO (30 atm)/CO$_2$ (5 atm) resulted in the formation of **2a** in 93% yield (entry 2). In contrast, the reaction under CO$_2$ (5 atm) did not afford the product **2a** (entry 3).
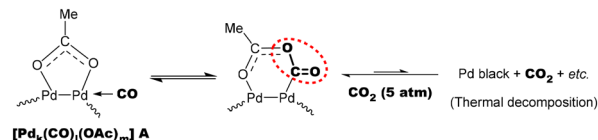
It has been reported that heating Pd$_4$(CO)$_4$(OAc)$_4$ above 100 °C led to the insertion of CO into the Pd–acetate bond, and the thermal decomposition proceeded irreversibly *via* the

Table 4 Control experiments using **A** (*in situ* generated) as the catalyst for the direct carbonylation of 2-ethylthiophene **1a**[a]

Entry	CO (atm)	CO$_2$ (atm)	Yield of **2a** (%)
1	30	—	66
2	**30**	**5**	93
3	—	5	N. D.

[a] Yields were determined by ^{1}H NMR spectroscopy.

Scheme 2 Proposed reversible reactions that could account for the thermal stability of **A** under CO/CO$_2$.

reductive elimination of the formed unstable palladium species along with the release of CO$_2$, resulting in the formation of inactive palladium black.[12,13] On the other hand, the developed catalytic reactions in this study proceeded well under the CO/CO$_2$-binary system, suggesting that CO$_2$ pressurization suppressed the above thermal decomposition and improved the stability and thermal durability of complex **A** (Scheme 2).

To clarify the effect of CO$_2$ on the reactions, we next attempted to synthesize **A** from Pd(OAc)$_2$ under pressurized CO conditions in AcOH. When the solution of Pd(OAc)$_2$ in AcOH was heated at 100 °C for 15 min under CO (10 atm), an insoluble black solid (palladium black) was formed and complex **A** was obtained in trace amounts (eqn (6) in Fig. 2).[14] On the other hand, the reaction under CO (10 atm)/CO$_2$ (5 atm) in AcOH successfully led to the formation of **A**, which was confirmed by IR spectroscopy (eqn (7) in Fig. 2). Thus, it was clearly demonstrated that pressurized CO$_2$
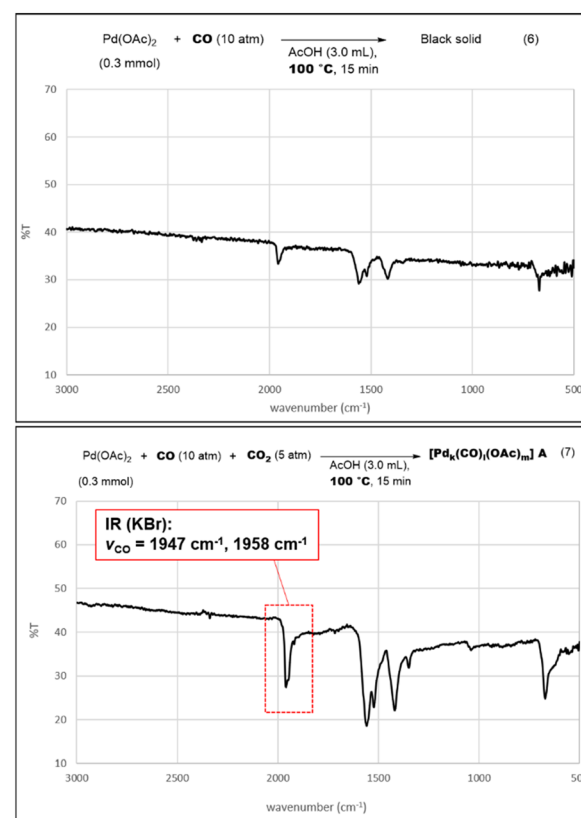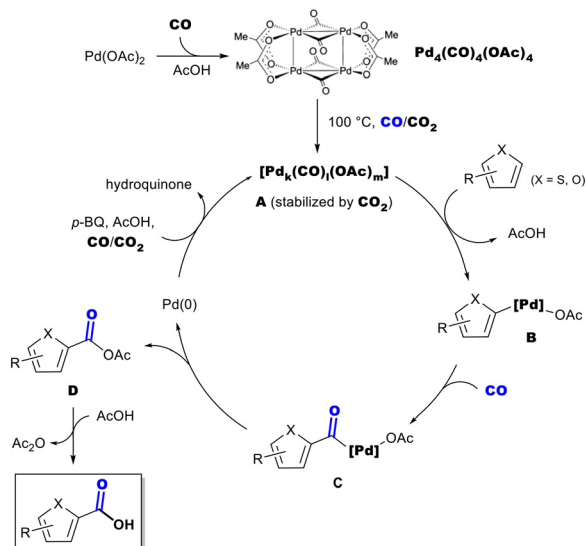

Fig. 2 IR spectra of the solids obtained from the reactions of Pd(OAc)$_2$ with CO in AcOH.

Scheme 3 A possible reaction pathway for Pd-catalyzed carbonylation of thiophenes and furans under CO/CO_2-binary conditions.

suppressed the thermal decomposition of **A** to inactive palladium black and improved the durability of **A** under reaction conditions.

Based on these insights and previous studies, a possible reaction pathway for Pd-catalyzed direct carbonylation of thiophenes and furans is proposed, as indicated in Scheme 3. Initially, $Pd(OAc)_2$ reacts with CO to form $Pd_4(CO)_4(OAc)_4$. Then, the following partial thermal decomposition of $Pd_4(CO)_4(OAc)_4$ occurs and complex **A** is generated, which is stabilized by pressurized CO_2. Subsequently, the C–H bond activation of thiophenes or furans by **A** leads to arylpalladium(II) species **B** via concerted metalation–deprotonation processes, in which the C–Pd bond formation proceeds along with the generation of AcOH.[15–18] Insertion of CO into the C–Pd bond of **B** forms **C**, and the following reductive elimination affords **D** with Pd^0. Finally, the protonation/deacetylation of **D** in AcOH gives the corresponding carboxylic acids. Pd^0 could be oxidized by *p*-BQ in AcOH under CO/CO_2-binary conditions, and the catalytically active species **A** could be regenerated.

Conclusions

In summary, we have developed novel palladium-catalyzed direct carbonylation of thiophenes and furans under CO/CO_2-binary conditions, leading to the corresponding carboxylic acids in up to quantitative yields. Conventional palladium-promoted direct carbonylation of heteroaromatics was difficult to conduct as a catalytic reaction due to the thermal decomposition of palladium active species. In contrast, in this study, we found for the first time that the thermal decomposition of the catalyst could be suppressed by producing a more active catalytic species under CO/CO_2-

binary conditions; thus, highly efficient conversion of thiophenes and furans to the corresponding carboxylic acids has been attained with only 1 mol% catalyst loading. Direct and catalytic carbonylation has been considered one of the most challenging reactions; therefore, the method established in this study will lead to a novel, practical, and versatile transformation based on direct carbonylation. We believe that this catalytic system will provide novel eco-friendly synthetic strategies toward multi-functionalization in organic synthesis. Further investigation of reaction mechanisms, catalytic carbonylation of other aromatic compounds, and application to the synthesis of functional molecules are currently ongoing.

Data availability

The ESI† includes all experimental procedures, characterisation data, and NMR spectra of **2a–2o**, **4b–4d**, and **4f–4j**.

Author contributions

Conceptualization: Y. Y., D. K. and A. O.; data curation: Y. Y and A. O.; formal analysis: Y. Y. and D. K.; funding acquisition: Y. Y. and A. O.; investigation: Y. Y., D. K. and A. O.; methodology: Y. Y., D. K., and A. O.; project administration: A. O.; resources: Y. Y., D. K. and A. O.; supervision: A. O.; validation: Y. Y. and A. O.; writing – original draft: Y. Y. and A. O.; writing – review & editing: Y. Y. and A. O. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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