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One-Pot Synthesis of 2,5-Furandicarboxylic Acid from 2-Furoic Acid by a Pd-catalyzed Bromination–Hydroxycarbonylation Tandem Reaction in Acetate Buffer

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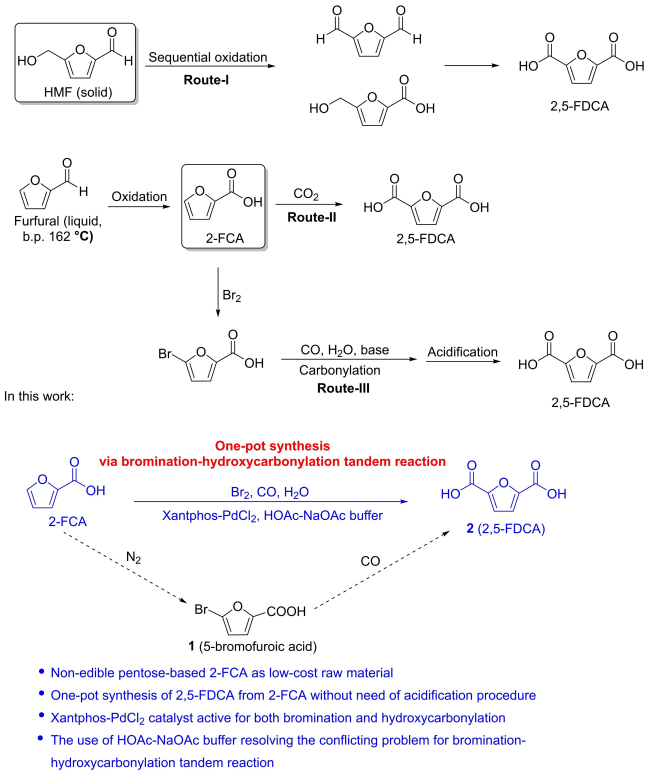
The one-pot synthesis of 2,5-furandicarboxylic acid from 2-furoic acid with a yield of 57% was achieved for the first time using a Pd-catalyzed bromination-hydroxycarbonylation tandem reaction in HOAc-NaOAc buffer. This synthetic protocol shows major improvements compared to previously reported methods, such as using biomass-based 2-furoic acid as low-cost raw material, one-pot synthesis without isolation of intermediate products, and no need for an acidification procedure. Experiments indicate that the involved Xantphos-modified Pd-catalyst and the buffer solution play significant promoting roles for each individual reaction whereas Br_2 (as the brominating reagent) had a negative effect on the second hydroxycarbonylation step, while CO was deleterious for the first bromination step. Hence, in this practical one-pot synthesis, Br_2 should be consumed in the first bromination step as fully as possible, and CO is introduced after the first bromination step has been completed.

Introduction

The production of bio-based 2,5-furandicarboxylic acid (2,5-FDCA) has attracted much attention in the recent decade due to its versatility as an important bio-based platform chemical as well as the concern to decrease the dependence on fossil feedback to produce chemicals.[1,2] 2,5-FDCA has proved itself a suitable monomer for the synthesis of polymers, such as poly(ethylene furandicarboxylate) (PEF), a potential polymer used in soft drink bottling,[3] which might be a replacement for the fossil-derived poly(ethylene terephthalate) (PET). In the literature, there are three main routes for the synthesis of 2,5-FDCA as summarized in Scheme 1. Route-I involves oxidation of 5-(hydroxymethyl) furfural (HMF) to 2,5-FDCA through a number of thermal-catalytic,[4–10] electrocatalytic,[11] photocatalytic[12] and biocatalytic[13–15] processes. Thereinto, sequential oxidation of the two functional groups (formyl and hydroxyl) bound to the furan ring leads to the formation of 2,5-FDCA. Although this reaction route has been widely studied, the low selectivity of 2,5-FDCA is still a concerning problem due to the formation of many unstable intermediate products as well as the lability of HMF itself.[1,2,16] Moreover, HMF, generally obtained from edible fructose in conflict with food industry, is required to be of very high purity but is quite difficult to be purified as a solid compound. Route-II and Route-III pertain to furfural or its downstream product being converted into 2,5-FDCA. The industrial production of furfural from non-edible pentose (derived from hemicellulose) is a mature process. The production of 2-furancarboxylic acid (2-FCA) from furfural oxidation using several heterogeneous catalysts is also well



Scheme 1. Different pathways for the synthesis of 2,5-FDCA.

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established.[17–21] Hence, 2-FCA is very suitable to replace HMF, and Route-II, carboxylation of 2-FCA by CO_2 into 2,5-FDCA, becomes an interesting protocol along with the increased concern on CO_2 utilization. This reaction only occurred from 200 to 350 °C with need of strongly alkaline salts in order to deprotonate the very weakly acidic C–H bond ($pK_a > 40$) to react with CO_2, but the reaction mechanism remains speculative.[16,22–25] In Route-III, carbonylation of 5-bromofuroic acid (as the derivative of 2-FCA) with CO and H_2O, was reported by Yin's group, wherein 2,5-FDCA was obtained with excellent selectivity under mild conditions using homogenous and heterogenous Pd- catalysts, respectively.[26–29] In addition, the Henkel-type disproportion[30–32] of potassium-2-furoate at 260 °C in the presence of Lewis-acidic catalysts like CdI_2 or $ZnCl_2$ to form 2,5-FDCA and furan was firstly reported by D. S. van Es.[33]

The use of fructose as the starting material instead of HMF in the synthesis of 2,5-FDCA through stepwise oxidation processes further enhanced the reaction complexity, which required more elaborately designed catalytic systems and engineering techniques.[34–37] Accordingly, not only the applied catalysts in the mode of conventional heating or electro-/photo-initiation, but also the selection of the bio-derived raw materials determines the practicability and diversity in the synthesis of 2,5-FDCA.

Inspired by Yin's work as well as our continuous interest in carbonylation using ligand-modified Pd catalysts, in this work, we explored the one-pot bromination-hydroxycarbonylation tandem reaction for the synthesis of 2,5-FDCA acid from 2-FCA, which is an unprecedented transformation in the literature. In the reaction sequence, the bromination of 2-FAC by brominating reagent such as liquid bromine (Br_2) goes by the very well established acid-catalyzed electrophilic aromatic substitution mechanism, whereas the hydroxycarbonylation of 5-bromofuroic acid (**1**) with CO and water occurs in the presence of a phosphine-modified Pd catalyst with presence of base. Evidently, in this one-pot sequence, the acid is required for the first bromination step and the base is required for second step, which are totally conflicting conditions. In order to solve this problem, a buffer solution composed of HOAc and NaOAc with pH range of 3.0 to 4.0 was applied in this work, which proved workable not only in the way to enable each individual reaction performing efficiently but to also directly yield the product, 2,5-FDCA, without the need for acidification.

Results and Discussion

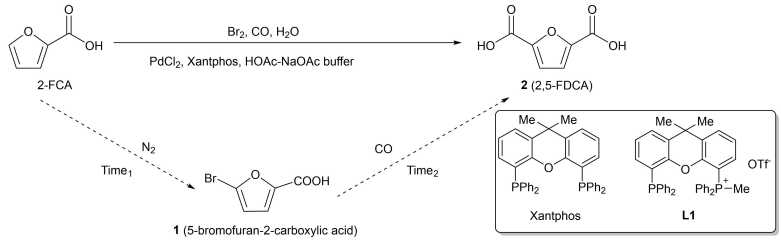
We initiated our studies by carrying out the optimization of reaction conditions for one-pot bromination-carbonylation tandem reaction for the synthesis of 2,5-FDCA (**2**) from 2-FCA, which was catalyzed by Xantphos-modified $PdCl_2$ (Table 1). $PdCl_2$ was identified as the best choice of catalyst precursor. The mild reaction temperature of 90 °C was required as otherwise many unidentified sideproducts coming from ring-opening reactions of 2-FCA and the products (**1** and **2**) were formed.

The excess Br_2 of two equivalents was required to guarantee the first bromination step of 2-FCA towards 5-bromofuran-2-carboxylic acid (**1**) (Entry 2 vs. 1). It was found that the presence of CO (1.0 MPa) dramatically reduced the yield of target product **2** due to the inhibited bromination of 2-FCA in the CO atmosphere (Entry 3 vs. 2). Hence, an N_2 atmosphere (0.1 MPa) was applied for the first bromination step, and CO (1.0 MPa) was followingly introduced for the second carbonylation step. The long reaction time of 10 h was needed for this N_2-protected bromination and a shorter time of 2 h was found sufficient for the second carbonylation step (Entries 2, 4, 5 vs. 6 and 7). Longer reaction times of up to 12 h just resulted in the prevailing of the ring-opening reaction of **1**, leading to a decreased selectivity for **2** in the overall tandem process (Entry 4 vs. 2). Less water resulted in higher selectivity for **2** (Entry 8 vs. 7). A solvent screening showed that DMF was the best solvent, corresponding to the highest yield of **2** (Entry 8, 57%). The use of THF, NMP or no solvent led to comparable conversions of 2-FCA but at much lower selectivity for **2** (Entries 8 vs. 9–11). A decreased concentration of the Pd catalyst led to the obviously diminished selectivity of **2** (Entry 8 vs. 12), implying that the involved Xantphos-modified $PdCl_2$ catalyst also contributed to the first bromination step of 2-FCA since just the success of this bromination could warrant the subsequent carbonylation ensuing smoothly.

With these established optimal reaction conditions, the ligand effect on the reaction efficiency was investigated. When **L1** with the same xanthenyl-skeleton but as a mono-phosphine was applied instead of the bisphosphine Xantphos, a comparable yield of **2** of 55% was obtained (Entry 13 vs. 8) whereas the use of the mono-phosphine PPh_3 just corresponded to a much lower yield of 36% (Entry 14). However, an increased amount of Xantphos led to a drop in selectivity for **2** despite no dramatic effect on 2-FCA conversion (Entry 15). Using NaBrO instead of Br_2 as brominating reagent led to a comparable yield of **2** with an improved selectivity of 81% despite a relatively lower conversion of 2-FCA (Entry 16 vs. 8). Besides, the use of NBS (*N*-bromosuccinimide) or $TBABr_3$ (tetrabutylammonium tribromide) corresponded to an extremely low selectivity for **2** due to the prevailing furan-ring-opening side-reactions (Entries 17 and 18). In comparison to $Pd(OAc)_2$ and $Pd(CH_3CN)Cl_2$ as catalyst precursors, $PdCl_2$ resulted in a much higher yield of **2** (Entries 8 vs. 19 and 20), presumably due to the in situ formed acidic HCl derived from the reaction of $PdCl_2$ and HOAc favoring the first bromination step. Additionally, when sodium 2-furoate was applied as the staring material, a nearly identical outcome was obtained in comparison to 2-FCA (Entry 21 vs. 8). Since buffer solution composed of NaOAc (6 mmol) and (HOAc 87 mmol) was involved in excess, 2-FCA and its sodium salt always co-existed in this reaction system regardless of whether 2-FCA (2 mmol) or sodium 2-furoate (2 mmol) were used as the starting materials.

In general, an acid is required as the catalyst for classical bromination of aromatic compounds. A base is required as the scavenger for hydroxycarbonylation of aryl bromides. Hence, in this studied bromination-hydroxycarbonylation sequence, the sole presence of acid (HOAc) or base (NaOAc) nearly shut down

Table 1. Palladium-catalyzed bromination-hydroxycarbonylation tandem reaction for synthesis of 2,5-FDCA (**2**) from 2-FCA.[a]

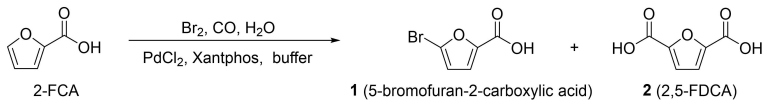


Entry	$Time_1$ [h]	$Time_2$ [h]	Amount of brominating reagent [mmol]	H_2O [mmol]	Solvent	Ligand	Conv. [%][b]	Sel. of **1** [%][b]	Sel. of **2** [%][b]	Yield of **2** [%][b]
1	12	12	3 (Br_2)	50	DMF	Xantphos	67	2	42	28
2	12	12	4 (Br_2)	50	DMF	Xantphos	90	1	50	45
3[c]	12	12	4 (Br_2)	50	DMF	Xantphos	77	0	17	13
4	10	12	4 (Br_2)	50	DMF	Xantphos	88	1	60	53
5	8	12	4 (Br_2)	50	DMF	Xantphos	83	1	49	43
6	10	4	4 (Br_2)	50	DMF	Xantphos	88	1	57	50
7	10	2	4 (Br_2)	50	DMF	Xantphos	73	0	67	49
8	10	2	4 (Br_2)	5	DMF	Xantphos	77	2	74	57
9	10	2	4 (Br_2)	5	THF	Xantphos	81	1	31	25
10	10	2	4 (Br_2)	5	NMP	Xantphos	80	2	31	25
11	10	2	4 (Br_2)	5	–	Xantphos	85	1	18	15
12[d]	10	2	4 (Br_2)	5	DMF	Xantphos	77	2	48	37
13[e]	10	2	4 (Br_2)	5	DMF	**L1**	79	11	70	55
14[f]	10	2	4 (Br_2)	5	DMF	PPh_3	72	3	50	36
15[g]	10	2	4 (Br_2)	5	DMF	Xantphos	71	3	44	31
16	10	2	4 (NaBrO)	5	DMF	Xantphos	69	5	81	56
17[h]	10	2	4 (NBS)	5	DMF	Xantphos	86	0	5	4
18[i]	10	2	4 ($TBABr_3$)	5	DMF	Xantphos	78	1	7	6
19[j]	10	2	4 (Br_2)	5	DMF	Xantphos	50	0	38	19
20[k]	10	2	4 (Br_2)	5	DMF	Xantphos	57	2	47	27
21[l]	10	2	4 (Br_2)	5	DNF	Xantphos	75	1	75	56

[a] 2-FCA 2 mmol, $PdCl_2$ 5 mol%, ligand 5 mol%, NaOAc 6 mmol, HOAc 87 mmol, solvent 5 mL, 90 °C. N_2 (0.1 MPa) was charged initially for the first step reaction and CO (1.0 MPa) was then charged after $time_1$ for the second step reaction; [b] determined by HPLC. Many kinds of ring-opening side products were found but could not be identified; [c] CO (1.0 MPa) was always present during the overall tandem reaction; [d] $PdCl_2$ 2 mol%, Xantphos 2 mol%; [e] **L1** 10 mol%; [f] PPh_3 10 mol%; [g] Xantphos 10 mol%; [h] NBS, *N*-Bromosuccinimide; [i] $TBABr_3$, tetrabutylammonium tribromide; [j] $Pd(OAc)_2$ 5 mol%; [k] $Pd(CH_3CN)_2Cl_2$ 5 mol%; [l] sodium 2-furoate (2 mmol) applied instead of 2-FCA.

the tandem reaction (Entries 1 and 2 of Table 2). The use of a buffer solution composed of HOAc and NaOAc with pH 3.58 was proven to be an effective strategy to resolve the conflicting problem for this sequence. As indicated in Table 2, the selectivity towards **2** was sensitive to the pH value of the involved buffer. Increasing the pH value of HOAc-NaOAc buffer

Table 2. The effect of pH value of the buffer on Pd-catalyzed bromination-hydroxycarbonylation tandem reaction for synthesis of 2,5-FDCA (**2**) from 2-FCA.[a]

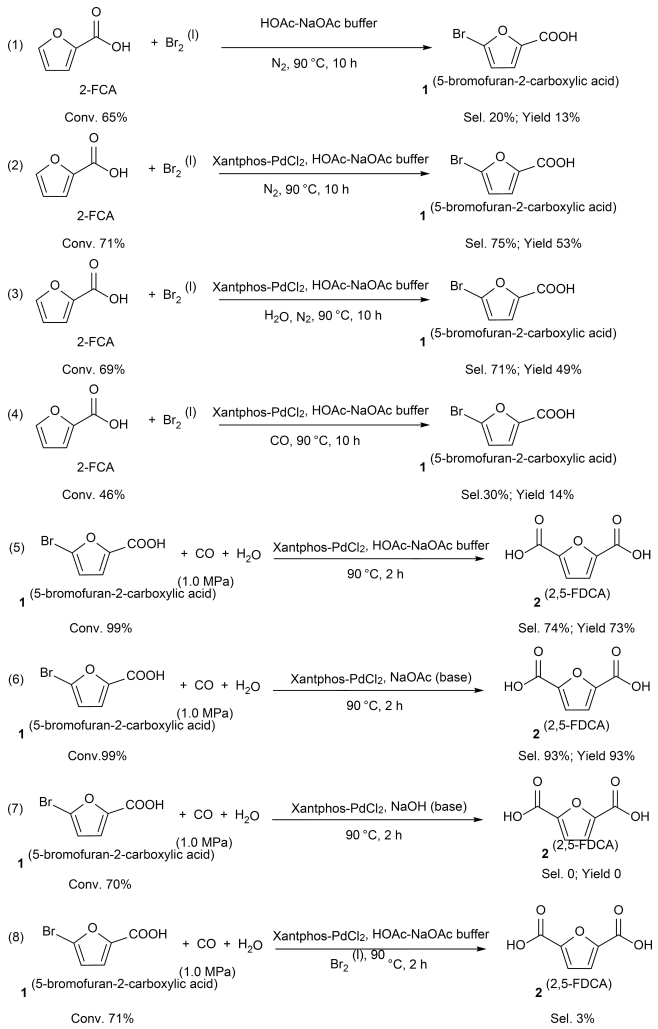


Entry	Buffer Acid (amount [mmol])	Salt (amount [mmol])	pH value	Conv. [%][b]	Sel. of **1** [%][b]	Sel. of **2** [%][b]	Yield of **2** [%][b]
1	–	NaOAc (6)	9.88[c]	61	8	13	8
2	HOAc (87)	–	2.50[d]	70	6	21	15
3	HOAc (87)	NaOAc (6)	3.58[e]	73	0	67	49
4	HOAc (33)	NaOAc (6)	4.00[e]	77	1	32	25
5	HOAc (10)	NaOAc (6)	4.50[e]	69	0	25	17
6	HOAc (3.3)	NaOAc (6)	5.00[e]	68	0	19	13
7	HOAc (330)	NaOAc (6)	3.00[c]	83	1	55	46
8	HOAc (87)	NH_4OAc (6)	3.50[c]	77	1	66	51

[a] 2-FCA 2 mmol, $PdCl_2$ 5 mol%, Xantphos 5 mol%, Br_2 4 mmol, H_2O 50 mmol, DMF 5 mL, 90 °C, $time_1 = 10$ h, $time_2 = 2$ h. N_2 (0.1 MPa) was charged initially for the first reaction step and CO (1.0 MPa) was then charged after 10 h for the second reaction step; [b] fetermined by HPLC. Many kinds of ring-opening side products were found but could not be identified; [c] in saturated aqueous solution of NaOAc (25 °C); [d] in pure HOAc (25 °C); [e] the pH value is calculated according to the equation of $pH = pK_a + lg[C_{salt}/C_{acid}]$ ($pK_a = 4.74$, representing the pK_a value of HOAc at 25 °C; C_{salt} is defined as the concertation of the salt; C_{acid} is defined as the concertation of the acid.

from 3.58 up to 5.00 dramatically decreased the selectivity towards **2**, leading to lowered yields (Entry 3 vs. 4–6). However, the decrease of the pH value of the HOAc-NaOAc buffer from 3.58 down to 3.00 also reduced the selectivity for **2** due to the prevalence of the competitive furan-ring-opening reactions under the stronger acidic conditions (Entry 3 vs. 7). The use of an HOAc-NH_4OAc buffer in place of HOAc-NaOAc with pH 3.50 led to a similar yield for **2** (Entry 3 vs. 8).

In order to demonstrate the (positive/negative) influences of the involved Br_2, CO, and Xantphos-$PdCl_2$ catalyst on each individual reaction, the bromination of 2-FCA and the hydroxycarbonylation of **1** (5-bromofuran-2-carboxylic acid) with CO and H_2O were separately carried out under controlled conditions (Scheme 2). When the bromination of 2-FCA by Br_2 was performed under an N_2-atmosphere with presence of HOAc-NaOAc buffer in DMF, only 13% yield of the brominated product **1** was obtained. The consumed 2-FCA was mostly converted into products related to the furan-ring-opening reaction of 2-FCA [Scheme 2-(1)]. In comparison, under the same conditions, when the catalyst of Xantphos-$PdCl_2$ presumed to only be responsible for second hydroxycarbonylation step of **1** was involved, the efficiency of the bromination of 2-FCA by Br_2 was dramatically improved, resulting in 75% selectivity for **1** with 53% yield [Scheme 2-(2)]. This outcome indicated that the Xantphos-$PdCl_2$ catalyst also exhibited significant activity in the bromination of 2-FCA along with the acidic HOAc-NaOAc buffer. The control experiment in Scheme 2-(3) demonstrated that the presence of water in small amounts (2.5 equiv. with respect to 2-FCA), which was required as the substrate in the hydroxycarbonylation, had a negligible effect on the bromination of 2-FCA towards **1**. However, the presence of CO (1.0 MPa) almost stopped the bromination to deliver **1** [Scheme 2-(4)], possibly due to the in situ coordination of CO to the Pd center to quench the catalytic performance of $PdCl_2$ as a Lewis-acidic catalyst, which was consistent with the result in entry 3 of Table 1. Hence, in the practical bromination-hydroxycarbonylation tandem reaction, the first bromination step should be performed without a CO-atmosphere as shown in Tables 1 and 2. On the other hand, the independent hydroxycarbonylation of **1** with CO and H_2O was carried out as shown in Scheme 2-(5–8) under different conditions. It was indicated that the hydroxycarbonylation of **1** in the presence of HOAc-NaOAc as an acid-scavenger afforded **2** in the yield of only 73% despite 99% conversion of **1**, wherein the complicated and unidentified side products were found due to furanyl-ring-opening reactions of **1** and **2** [Scheme 2-(5)]. In comparison, the use of NaOAc instead of HOAc-NaOAc to repeat the reaction led to 93% yield of **2** along with 99% conversion of **1** [Scheme 2-(6)], which implied that the acidity of HOAc-NaOAc indeed would drive the furan-ring-opening reaction to happen in parallel. However, the use of NaOH, a stronger base, in place of NaOAc stopped the expected hydroxycarbonylation due to the prevailing hydrolysis of furan-ring of **1** [Scheme 2-(7)]. Similarly, the presence of Br_2 also shut down the expected carbonylation due to the severe oxidative degradation of **1** by Br_2 [Scheme 2-(8)]. Hence, it was suggested that the involved Br_2 should be exhausted completely in the first-step bromination of 2-FCA in order to rule out its negative effect on the second-step hydroxycarbonylation of **1**.



Scheme 2. Control experiments (reaction conditions: substrate 2 mmol, $PdCl_2$ 5 mol%, Xantphos 5 mol%, Br_2 4 mmol, NaOAc 6 mmol, HOAc 87.4 mmol, H_2O 5 mmol, DMF 5 mL; N_2 pressure 0.1 MPa, CO pressure 1.0 MPa; Conv.% and Sel.% were determined by HPLC.)

Conclusion

This work presents the one-pot bromination-hydroxycarbonylation tandem reaction for synthesis of 2,5-FDCA from 2-FCA for the first time. Under the optimal conditions, 2,5-FDCA was obtained in the yield of 57% without the need of acidification procedure. The use of HOAc-NaOAc buffer with pH 3.58 resolves the conflicting problem for bromination-hydroxycarbonylation sequence. It has been found that the involved Xantphos-modified Pd catalyst and HOAc-NaOAc buffer solution played significant promoting role for each individual reaction whereas Br_2 (as the brominating reagent) had negative effect on the second-step hydroxycarbonylation, and CO was a poison for the first-step bromination. Hence, in this practical one-pot synthesis, Br_2 should be consumed in the first-step bromination as flly as

possible, and CO is charged after the first bromination step has been completed.

Experimental Section

Reagents and Analyses

Chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai Aladdin Chemical Reagent Co., Ltd. and Adamas Reagent, Ltd., which were used as received. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker ARX 500 spectrometer at ambient temperature. The product analysis was conducted on a HPLC (ECHCOMP) instrument with the external standard method at ambient temperature. The HPLC instrument was equipped with an UV-detector with wavelength of 254 nm and a C8 column (250 mm × 4.6 mm). The mobile phase was composed of H_2O, CH_3CN and HOAc by the ratio of 90%:10%:1‰ (v/v/v) and the flowing rate was 1 mL min^{-1}. The pH value was determined by a pH meter (PHS-3 C).

Synthetic Procedures

Synthesis of L1

L1 was prepared according to the procedures described in our previous work.[38]

General Procedure for the Bromination–Hydroxycarbonylation Tandem Reaction of 2-FCA

In a typical experiment, $PdCl_2$ (0.1 mmol), ligand (0.1 mmol), 2-FCA (2 mmol), NaOAc (6 mmol), HOAc (87 mmol), solvent (5 mL), H_2O (5 mmol) and Br_2 (4 mmol) were sequentially added to a 50 mL sealed Teflon-lined stainless-steel autoclave, which was purged three times with N_2 (0.3 MPa). The reaction mixture in the sealed autoclave was stirred at 500 rpm and 90 °C for 10 h at N_2-atmospheric pressure, then cooled down to room temperature. Then, the autoclave was pressurized with CO to 1.0 MPa after purging with CO for three times. Then, the reaction mixture was stirred at 500 rpm and 90 °C for 2 h. Upon completion, the autoclave was cooled down to room temperature and slowly depressurized. The obtained mixture was analysed by HPLC using the external standard method.

General Procedure for Separate Bromination of 2-FCA

In a typical experiment, $PdCl_2$ (0.1 mmol, if required), Xantphos (0.1 mmol, if required), 2-FCA (2 mmol), NaOAc (6 mmol), HOAc (87 mmol), solvent (5 mL), H_2O (5 mmol, if required) and Br_2 (4 mmol) were sequentially added to a 50 mL sealed, Teflon-lined stainless-steel autoclave, which was purged with N_2 (0.3 MPa). The reaction mixture in the sealed autoclave was stirred at 500 rpm and 90 °C for 10 h at N_2-atmospheric pressure, then cooled down to room temperature. The obtained mixture was analysed by HPLC using the external standard method.

General Procedure for Separate Hydroxycarbonylation of 5-Bromofuran-2-carboxylic Acid

In a typical experiment, $PdCl_2$ (0.1 mmol), Xantphos (0.1 mmol), 5-bromofuran-2-carboxylic acid (2 mmol), NaOAc (6 mmol), HOAc (87 mmol), solvent (5 mL), H_2O (5 mmol) and Br_2 (4 mmol if required) were sequentially added to a 50 mL sealed Teflon-lined stainless-steel autoclave, which was purged three times with CO (0.3 MPa) and pressurized with CO to 1.0 MPa. Then, the reaction mixture in the sealed autoclave was stirred at 500 rpm and 90 °C for 2 h. Upon completion, the autoclave was cooled down to room temperature and slowly depressurized. The obtained mixture was analysed by HPLC using the external standard method.

^{1}H and ^{13}C NMR characterizations of 2,5-FDCA ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.61 (s, 2H, ArCOO**H**), 7.30 (s, 2H, Ar**H**). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 159.35, 147.48, 118.87 (Copies of the ^{1}H/^{13}C NMR spectra are provided in the Supporting Information).

^{1}H and ^{13}C NMR characterizations of 5-bromofuran-2-carboxylic acid ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.34 (s, 1H, ArCOO**H**), 7.25 (d, J = 3.5 Hz, 1H), 6.81 (d, J = 3.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 158.70, 147.25, 127.21, 120.54, 114.83 (Copies of the ^{1}H/^{13}C NMR spectra are provided in the Supporting Information).

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: bromination · 2,5-furandicarboxylic acid · 2-furoic acid · hydroxycarbonylation · tandem reaction

[1] S. P. Teong, G. Yi, Y. Zhang, *Green Chem.* **2014**, *16*, 2015–2026.
[2] R.-J. Van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499–1597.
[3] Casanova, S. Iborra, A. Corma, Mécanisme, *J. Catal.* **2009**, *265*, 109–116.
[4] Schade, P. Dolcet, A. Nefedov, X. Huang, E. Saraçi, C. Wöll, J.-D. Grunwaldt, *Catalysts* **2020**, *10*, 342, 1–13.
[5] R. Schade, F. Stein, S. Reichenberger, A. Gaur, E. Saraçi, S. Barcikowski, J.-D. Grunwaldt, *Adv. Synth. Catal.* **2020**, *362*, 5681–5696.
[6] D. Bonincontro, A. Lolli, A. Villa, L. Prati, N. Dimitratos, G. M. Veith, L. E. Chinchilla, G. A. Botton, F. Cavani, S. Albonetti, *Green Chem.* **2019**, *21*, 4090–4099.
[7] N. K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, *Green Chem.* **2011**, *13*, 824–827.
[8] A. B. Gawade, A. V. Nakhate, G. D. Yadav, *Catal. Today* **2018**, *309*, 119–125.
[9] C. Chen, X. Li, L. Wang, T. Liang, L. Wang, Y. Zhang, J. Zhang, *ACS Sustainable Chem. Eng.* **2017**, *5*, 11300–11306.
[10] Z. Gui, W. Cao, S. Saravanamurugan, A. Riisager, L. Chen, Z. Qi, *ChemCatChem* **2016**, *8*, 3636–3643.
[11] L. Gao, S. Gan, J. Ma, Z. Sun, Z. Liu, L. Zhong, K. Zhou, F. Han, W. Wang, D. Han, L. Niu, *ChemElectroChem* **2020**, *7*, 4251–4258.
[12] S. Xu, P. Zhou, Z. Zhang, C. Yang, B. Zhang, K. Deng, S. Bottle, H. Zhu, *J. Am. Chem. Soc.* **2017**, *139*, 14775–14782.
[13] W. P. Dijkman, D. E. Groothuis, M. W. Fraaije, *Angew. Chem. Int. Ed.* **2014**, *53*, 6515–6518; *Angew. Chem.* **2014**, *126*, 6633–6636.
[14] J. Viña-Gonzalez, A. T. Martinez, V. Guallar, *Biochim. Biophys. Acta Proteins Proteomics* **2020**, *1868*, 140293.

[15] H. Yuan, Y. Liu, J. Li, H. Shin, G. Du, Z. Shi, J. Chen, L. Liu, *Biotechnol. Bioeng.* **2018**, *115*, 2148–2155.
[16] F. Drault, Y. Snoussi, J. Thuriot-Roukos, I. Itabaiana Jr., S. Paul, R. Wojcieszak, *Catalysts* **2021**, *11*, 326.
[17] Q. Tian, D. Shi, Y. Sha, *Molecules* **2008**, *13*, 948–957.
[18] C. D. Hurd, J. W. Garrett, E. N. Osborne, *J. Am. Chem. Soc.* **1933**, *55*, 1082–1084.
[19] E. Taarning, I. S. Nielsen, K. Egeblad, R. Madsen, C. H. Christensen, *ChemSusChem* **2008**, *1*, 75–78.
[20] F. Santarelli, R. Wojcieszak, S. Paul, F. Dumeignil, F. Cavani, *WO Pat.* 02017158106 A1, **2017**.
[21] C. P. Ferraz, A. G. M. D. Silva, T. S. Rodrigues, P. H. C. Camargo, S. Paul, R. Wojcieszak, *Appl. Sci.* **2018**, *8*, 1246.
[22] A. Banerjeel, G. R. Dick, T. Yoshino, M. W. Kanan, *Nature* **2016**, *531*, 216–219.
[23] Y.-G. Wang, C.-Y. Guo, J. Shen, Y.-Q. Sun, Y.-X. Niu, P. Li, G. Liu, X.-Y. Wei, *J. CO_2 Util.* **2021**, *48*, 101524.
[24] H. Zhou, H. Xu, X. Wang, Y. Liu, *Green Chem.* **2019**, *21*, 2923–2927.
[25] F. Nocito, N. Ditaranto, A. Dibenedetto, *J. CO2 Util.* **2019**, *32*, 170–177.
[26] S. Zhang, J. Lan, Z. Chen, G. Yin, G. Li, *ACS Sustainable Chem. Eng.* **2017**, *5*, 9360–9369.
[27] G. Shen, S. Zhang, Y. Lei, Z. Chen, G. Yin, *J. Mol. Catal.* **2018**, *455*, 204–209.
[28] S. Zhang, G. Shen, Y. Deng, Y. Lei, J. Xue, Z. Chen, G. Yin, *ACS Sustainable Chem. Eng.* **2018**, *6*, 13192–13198.
[29] G. Shen, J. Shi, Y. Lei, C. Fu, Z. Chen, B. Andrioletti, G. Yin, *Ind. Eng. Chem. Res.* **2019**, *58*, 22951–22957.
[30] B. Raecke, *Angew. Chem.* **1958**, *70*, 1.
[31] E. McNelis, *J. Org. Chem.* **1965**, *30*, 1209–1213.
[32] K. Kudo, M. Shima, Y. Kume, F. Ikoma, S. Mori, N. Sugita, *J. Jpn. Pet. Inst.* **1995**, *38*, 40–47.
[33] S. Thiyagarajan, A. Pukin, J. van Haveren, M. Lutz, D. S. van Es, *RSC Adv.* **2013**, *3*, 15678–15686.
[34] G. Chen, L. Wu, H. Fan, B Li, *Ind. Eng. Chem. Res.* **2018**, *57*, 16172–16181.
[35] G. Yi, S. P. Teong, Y. Zhang, *ChemSusChem* **2015**, *8*, 1151–1155.
[36] M. L. Ribeiro, U. Schuchardt, *Catal. Commun.* **2003**, *4*, 83–86.
[37] M. Kröger, U. Prüße, K.-D. Vorlop, *Top. Catal.* **2000**, *13*, 237–242.
[38] Xia Chen, Xu Ye, Wen-Yu Liang, Qing Zhou, Giang Vo-Thanh, Ye Liu, *J. Mol. Catal.* **2018**, *448*, 171–176.

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