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Oxalic acid as the *in situ* carbon monoxide generator in palladium-catalyzed hydroxycarbonylation of arylhalides†

Changdong Shao,[a,b] Ailan Lu,[a] Xiaoling Wang,[a] Bo Zhou,[a] Xiaohong Guan*[b,c] and Yanghui Zhang*[a,b,d]

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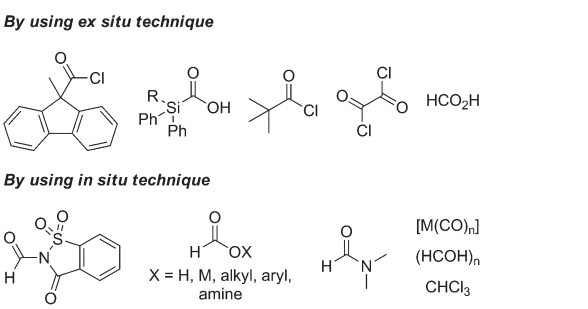
An efficient palladium-catalyzed hydroxycarbonylation reaction of arylhalides using oxalic acid as a CO source has been developed. The reaction features high safety, low catalyst loading, and a broad substrate scope, and provides a safe and tractable approach to access a variety of aromatic carboxylic acid compounds. Mechanistic studies revealed the decomposition pattern of oxalic acid.

Introduction

Carboxylic acids and their derivatives, such as esters, amides, *etc.*, are important intermediates and extensively exist in pharmaceuticals, perfumes, dyes, and other manufactured chemicals.[1] For instance, acetylsalicylic acid and niacin, with the trade name of aspirin and vitamin B_3 respectively, are worldwide commercialized medicines. Likewise, terephthalic acid is one of the synthons in the synthesis of the extremely famous polymer material Dacron. Carboxylic acids may be prepared in a simple manner by, for example, the oxidation of preoxidized substrates, hydrolysis of related derivatives, and the combination of carbon dioxide into nucleophilic reagents such as organolithium or organomagnesium halides.[2] Despite the high efficiency and low-cost advantages of these conventional procedures, harsh reaction conditions or high reactivity of reagents makes them inadequate in chemoselectivity or functional group tolerance. Thus, transition metal-catalyzed carbonylation reactions of halogenated hydrocarbons with carbon monoxide and various nucleophiles have been one of the most important methods to acquire complex carbonyl compounds that bear various functional groups.[3] The pioneering work in this field was reported by Heck more than 40 years ago.[4]

Although a plethora of carbonylation reactions in industry demonstrated the utility of CO gas, chemists are still reluctant to use it in laboratory. The reasons for this are no doubt related to the highly toxic, colorless, flavorless, and explosible properties of carbon monoxide, and in most cases specialized high-pressure equipment is also needed. To address these problems, lots of CO surrogates that can generate CO gas in an *in situ* or *ex situ* manner have been developed as the alternative proposal to avoid direct operation of CO gas (Scheme 1).[5] Skrydstrup and co-workers reported lots of examples by using 9-methylfluorene-9-carbonylchloride,[6] silacarboxylic acid,[7] and tertiary acid chloride[8] as the concentrated CO surrogates. Manabe's group published the palladium-catalyzed reductive carbonylation and fluorocarbonylation reactions of aryl halides using *N*-formylsaccharin as the CO source.[9] Many examples illustrated that formic acid and its derivatives can be treated as CO producers.[10] Metal carbonyl complexes,[11]



Scheme 1 Examples of generally used CO surrogates.

[a]*School of Chemical Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, P.R. China. E-mail: zhangyanghui@tongji.edu.cn; http://zhangyhgroup.tongji.edu.cn*
[b]*UNEP-Tongji Institute of Environment for Sustainable Development, Tongji University, 1239 Siping Road, Shanghai 200092, P.R. China*
[c]*College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, P. R. China*
[d]*Shanghai Key Laboratory of Chemical Assessment and Sustainability, 1239 Siping Road, Shanghai 200092, P.R. China*

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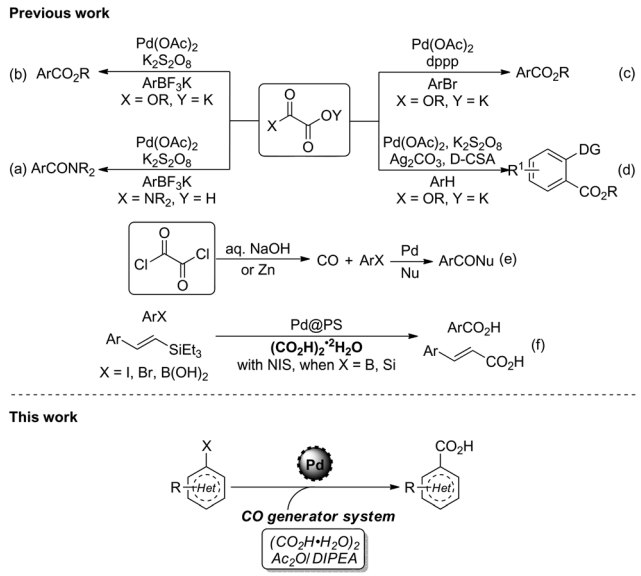
formaldehyde,[12] chloroform,[13] or even some alcohols[14] and carbohydrates[15] also can be regarded as CO succedaneums. Based on these CO surrogates, the "CO-free" carbonylation chemistry has made great breakthrough in the past few decades. However, drawbacks related to toxicity, price, stability, and atom efficiency still exist in front of chemists.

Oxalic acid and its derivatives are inexpensive, nontoxic, and abundant chemicals. Few examples have demonstrated that oxalic acid and its derivatives have the potential to be CO surrogates. Liu, Ge, and Wang reported several palladium-catalyzed decarboxylative cross-coupling reactions of potassium oxalate monoesters or oxamic acids with arylhalides, arylborates, and C–H bonds (Scheme 2a–d).[16] However, high reaction temperature or strong oxidizing agents are needed. Recently, Ulven and co-workers reported an example of using oxalyl chloride and NaOH aqueous solution to generate CO gas.[17] Almost simultaneously, Gracza *et al.* described a protocol for the generation of CO gas by the reduction of oxalyl chloride with zinc powder (e).[18] Oxalyl chloride is known as a deliquescent and amyctic liquid and should be operated with carefulness. Furthermore, the operation of a CO gas balloon or two-chamber apparatus still cannot be avoided in these two reports. Das and co-workers reported a palladium nanoparticle-catalyzed carboxylation of arylhalides. Despite the novelty of a palladium nanoparticle catalyst, the reaction was carried out under microwave irradiation with high temperature, pressure, excessive oxalic acid, and moderate yields (f).[19] Hence, developing facile and efficient carbonylation reactions using oxalic acid is still of great interest. Herein, we present an example of palladium-catalyzed hydroxycarbonylation reaction of arylhalides using oxalic acid as the operable concentrated carbonyl reagent.



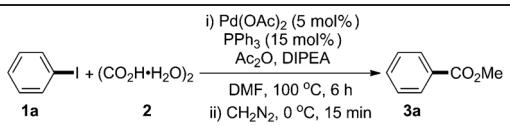
Scheme 2 Examples of using oxalic acid derivatives in carbonylation reactions.

Results and discussion

We initiated our research by investigating the hydroxycarbonylation of iodobenzene (**1a**). $(CO_2H{\cdot}H_2O)_2$, Ac_2O, and DIPEA were selected as the CO generator system (CO gen). Surprisingly, methyl benzoate (**3a**) was obtained in 94% yield when **1a** was treated with 5 mol% $Pd(OAc)_2$, 15 mol% PPh_3, and 3.0 equivalent CO gen in DMF at 100 °C for 6 hours followed by sequential esterification operation (Table 1, entry 1). The yield of **3a** decreased to 85% when the reaction time was reduced to 4 hours (entry 2). The decrease of reaction temperature also resulted in a slightly lower yield (entry 3). The impact of the ratios of the reagents on the reaction was investigated and the optimal conditions are summarized in Table 1 (entries 4 and 5, for details see the ESI†). Based on conditions C, further screening experiments were carried out, and the results illustrated that the catalyst loading can be lowered to 1 mol% (entry 6). Surprisingly, **3a** can also be generated with a satisfactory yield (89%) even when 0.5 mol% $Pd(OAc)_2$ was used (entry 7). Other palladium catalysts such as $Pd(PPh_3)_4$ (entry 8), $Pd(dba)_2$ and $Pd(PPh_3)_2Cl_2$ were also tested, and the results revealed that $Pd(OAc)_2$ was the optimal one (for details see the ESI†). The yield of **3a** decreased when anhydrous $(CO_2H)_2$ was used instead of $(CO_2H{\cdot}H_2O)_2$ (entry 9). Control experiments illustrated that $(CO_2H{\cdot}H_2O)_2$ and Ac_2O were indispensable components and DIPEA promotes the reaction tremendously (entries 10–13). No product was detected in the absence of $Pd(OAc)_2$ catalyst (entry 14).

With the optimal conditions in hand (entry 6), we next investigated the substrate scope of this hydroxycarbonylation

Table 1 Conditions screening



Entry	Variations from conditions X[a]	Yield[b] (%)
1	Conditions A	94
2	4 h instead of 6 h	85
3	80 °C instead of 100 °C	89
4	Conditions B	94
5	Conditions C	94
6	1 mol% $Pd(OAc)_2$ was used	94 (90)[c]
7	0.5 mol% $Pd(OAc)_2$ was used	89
8	$Pd(PPh_3)_4$ instead of $Pd(OAc)_2/PPh_3$	92
9	$(CO_2H)_2$ instead of $(CO_2H{\cdot}H_2O)_2$	84
10	Without $(CO_2H{\cdot}H_2O)_2$	—
11	Without Ac_2O	—
12	Without DIPEA	12
13	Without Ac_2O and DIPEA	—
14	Without $Pd(OAc)_2$	—

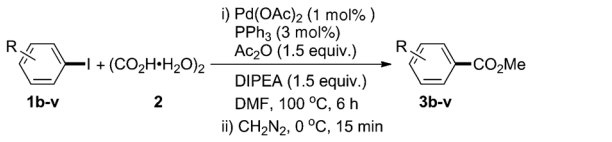
[a] Conditions A: PhI (0.2 mmol), $(CO_2H{\cdot}H_2O)_2$ (3.0 equiv.), Ac_2O (3.0 equiv.), DIPEA (3.0 equiv.). Conditions B: PhI (0.2 mmol), $(CO_2H{\cdot}H_2O)_2$ (2.5 equiv.), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.). Conditions C: PhI (0.4 mmol), $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.). [b] Yields were determined by ^1H NMR analysis of crude products using $C_2H_2Cl_4$ as the internal standard. [c] Isolated yield. DIPEA = *N*,*N*-diisopropylethylamine.

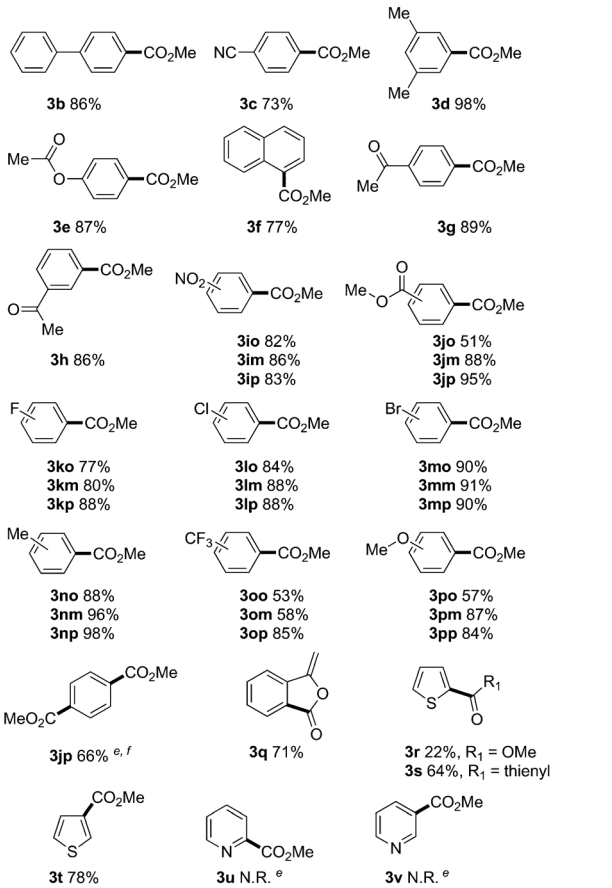
protocol. Gratifyingly, various substituted iodobenzenes (**1b–1v**) underwent the hydroxycarbonylation reaction efficiently, providing aromatic carboxylic acid esters (**3b–3v**) in moderate to excellent yields (Table 2). Both electron-withdrawing groups, such as cyano (**1c**), carbonyl (**1g**, **1h**), nitro (**1i**), ester (**1j**), and trifluoromethyl (**1o**), and electron-donating groups like methanoyl (**1e**), methyl (**1n**), and methoxyl (**1p**) were well-tolerated in the reaction. It should be noted that the halo groups, including F (**1k**), Cl (**1l**), and Br (**1m**), survived the reaction conditions. The protocol was applicable for a disubstituted substrate (**1d**), and 1-iodonaphthalene was also compatible (**1f**). To explore the applicability of the method in dual hydroxycarbonylation reactions, 1,4-diiodobenzene was selected as the reagent and dimethyl terephthalate (**3jp**) was observed in 66% yield. Surprisingly, when *o*-iodoacetophenone (**1q**) was used, methylphthalide (**3q**) rather than the corresponding carboxylate product was observed.[20] Notably, phthalide is the core framework of a series of chemical compounds (*e.g.* butylphthalide soft capsules, a useful medicine for the treatment of cerebral ischemia).[21] The reactivities of iodothiophenes (**1r** and **1t**) were also examined. Interestingly, the methyl 3-thiophenecarboxylate product (**3t**) was obtained in 78% yield when using 3-iodothiophene as the substrate while 2-iodothiophene gave dithiophenylketone (**3s**) as the main product together with only 22% methyl 2-thiophenecarboxylate (**3r**). However, iodopyridines (**1u**, **1v**) were incompatible with the reaction.

To disclose the reactivity of arylbromides, further screenings were carried out (for details see the ESI†). Bromobenzene (**4a**) underwent the hydroxycarbonylation reaction under a nitrogen atmosphere successfully by using xantphos as the ligand (Table 3). Arylbromides containing both electron-withdrawing groups (**4b–f**) and electron-donating groups (**4h–k**) exhibited high reactivity and the reactions were high yielding. The substrates bearing *ortho*-substituents such as chloro (**4g**) and methyl (**4ho**) groups gave the carboxylated products in lower yields. Bromo-substituted thiophenes (**4l** and **4m**) were also compatible and the desired products were formed in excellent yields. It should be noted that pyridine substrates (**4n** and **4o**) also underwent the carboxylation reaction, albeit in low yields.

To gain a better understanding of the reaction, a series of mechanistic studies were carried out. First of all, CO and CO_2 gas were detected by GC-TCD in an approximate 1 : 1 molar ratio after heating the CO generator system in DMF for 1 hour

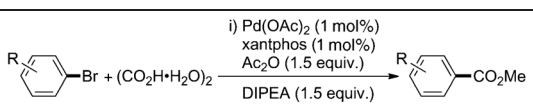
Table 2 Substrate scope of aryliodides[a,b,c,d]

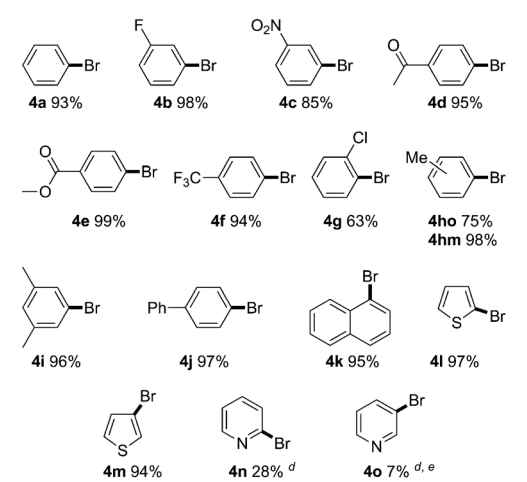




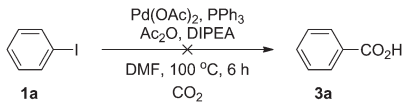
[a] Reaction conditions: Aryliodides (0.4 mmol), $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), $Pd(OAc)_2$ (1 mol%), PPh_3 (3 mol%), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.), DMF (2.0 mL), 100 °C, 6 h. [b] Treated with method A. [c] Isolated yield. [d] 3x*o*/*m*/*p* = *ortho*/*meta*/*para*-position. [e] Treated with method B. [f] 0.2 mmol 1,4-diiodobenzene was used.

Table 3 Substrate scope of arylbromides[a,b,c]

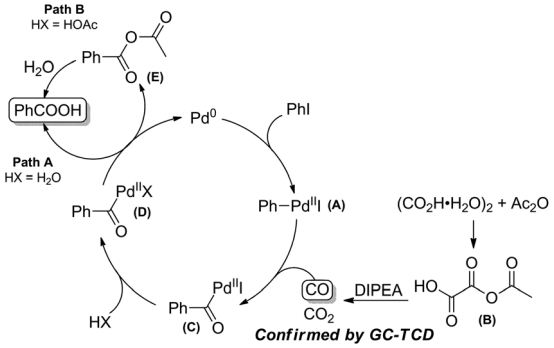




[a] Reaction conditions: Arylbromides (0.4 mmol), $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), $Pd(OAc)_2$ (1 mol%), xantphos (1 mol%), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.), DMF (2.0 mL), 100 °C, 6 h. [b] Treated with method A. [c] Isolated yield. [d] Treated with method B. [e] ^{1}H NMR yield. xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.



Scheme 3 Mechanistic study.



Scheme 4 Plausible mechanism.

(for details see the ESI†). Secondly, several reports demonstrated that CO_2 was an effective carboxylation reagent in Pd-, Ni-, and Cu-catalyzed carboxylation of aryl halides; however, no carboxylated product was detected in our catalytic system under a CO_2 atmosphere in the absence of $(CO_2H{\cdot}H_2O)_2$ (Scheme 3).[22] These results illustrated that CO, but not CO_2, was the carbon source in this hydroxycarbonylation reaction. Based on the mechanistic studies mentioned above and the literature,[23] a plausible mechanism pathway was suggested. As shown in Scheme 4, the oxidative addition of Pd(0) to aryl iodide gave arylpalladium complex **A**, and after the coordination and insertion of CO, which was generated by the decomposition of CO gen, acylpalladium intermediate **C** was formed. An acylpalladium complex **D** was subsequently generated after the ligand exchange with H_2O or HOAc. The final aromatic carboxylic acid was obtained after reductive elimination and meanwhile gave Pd(0) for the next catalyst cycle.

Conclusions

In conclusion, we have demonstrated that oxalic acid could be an inexpensive, nontoxic, abundant, and operable concentrated CO surrogate in palladium-catalyzed hydroxycarbonylation reactions of arylhalides. The protocol tolerates multiple functional groups and gave the corresponding aromatic carboxylic acid products in moderate to excellent yields. This method could also be applicable to the hydroxycarbonylation of heteroarylhalides.

Experimental section

General information

High resolution mass spectra were recorded on a Bruker MicroTOF II ESI-TOF mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX400. ^{1}H NMR spectra were recorded in $CDCl_3$ referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.00 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, and td = triplet of doublets. All the products were purified by flash column chromatography on silica gel (300–400 mesh) to give the corresponding compounds. All the reagents were used directly without further purification.

General procedures for hydroxycarbonylation

General procedures for the reactions of aryliodides. A 35 mL sealed tube equipped with a stir bar was charged with $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), $Pd(OAc)_2$ (1 mol%), PPh_3 (3 mol%), ArI (0.4 mmol), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.), and DMF (2.0 mL) in air. The tube was quickly sealed with a Teflon® high pressure valve. After the reaction mixture was stirred in a preheated oil bath (100 °C) for 6 h, it was allowed to cool down to room temperature.

General procedures for the reactions of arylbromides. A 35 mL Schlenk tube equipped with a stir bar was charged with $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), $Pd(OAc)_2$ (1 mol%), xantphos (1 mol%), ArBr (0.4 mmol), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.), and DMF (2.0 mL) in air. The tube was quickly sealed with a Teflon® high pressure valve, frozen in liquid nitrogen, evacuated and backfilled with N_2 (5 times). After the reaction mixture was stirred in a preheated oil bath (100 °C) for 6 h, it was allowed to cool down to room temperature.

Method A: The reaction mixture was diluted with EA (10 mL), acidified with 2 M HCl (5 mL, once), and washed with brine (5 mL, twice). The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The carboxylic acid product was then esterified with CH_2N_2 ether solution. The final ester products were purified by flash column chromatography on silica gel (300–400 mesh) to give the corresponding carboxylic acid ester compounds.

Method B: After being cooled down to room temperature, K_2CO_3 (4.0 equiv.) and CH_3I (4.0 equiv.) were added to the reaction mixture and stirred for another 6 h, then the mixture was diluted with EA (10 mL) and washed with brine (5 mL, twice). The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The final ester products were purified by flash column chromatography on silica gel (300–400 mesh) to give the corresponding carboxylic acid ester compounds.

Methyl benzoate 3a. 49.1 mg, 90% (for **1a**); 50.6 mg, 93% (for **4a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10, 132.88, 130.13, 129.54, 128.32, 52.07. HRMS (ESI-TOF) m/z: calcd for $C_8H_8NaO_2^+$: 159.0417 $(M + Na)^+$, found: 159.0416.

Methyl [1,1′-biphenyl]-4-carboxylate 3b. 73.0 mg, 86% (for **1b**); 82.3 mg, 97% (for **4j**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11

(d, J = 8.4 Hz, 2H), 7.65 (dd, J = 14.9, 7.9 Hz, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.98, 145.60, 139.96, 130.07, 128.89, 128.86, 128.11, 127.24, 127.01, 52.09. HRMS (ESI-TOF) m/z: calcd for $C_{14}H_{12}NaO_2^+$: 235.0730 $(M + Na)^+$, found: 235.0733.

Methyl 4-cyanobenzoate 3c. 47.0 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.41, 133.90, 132.20, 130.07, 117.93, 116.38, 52.70. HRMS (ESI-TOF) m/z: calcd for $C_9H_7NNaO_2^+$: 184.0369 $(M + Na)^+$, found: 184.0370.

Methyl 3,5-dimethylbenzoate 3d. 64.3 mg, 98% (for **1d**); 63.0 mg, 96% (for **4i**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.18 (s, 1H), 3.89 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.40, 137.95, 134.50, 129.96, 127.24, 51.92, 21.08. HRMS (ESI-TOF) m/z: calcd for $C_{10}H_{12}NaO_2^+$: 187.0730 $(M + Na)^+$, found: 187.0732.

Methyl 4-acetoxybenzoate 3e. 67.5 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.82, 166.26, 154.24, 131.12, 127.67, 121.56, 52.16, 21.11. HRMS (ESI-TOF) m/z: calcd for $C_{10}H_{10}NaO_4^+$: 217.0471 $(M + Na)^+$, found: 217.0469.

Methyl 1-naphthoate 3f. 57.3 mg, 77% (for **1f**); 70.7 mg, 95% (for **4k**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 8.6 Hz, 1H), 8.19 (d, J = 6.4 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.58–7.45 (m, 2H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.02, 133.81, 133.33, 131.30, 130.18, 128.51, 127.72, 127.06, 126.17, 125.78, 124.45, 52.11. HRMS (ESI-TOF) m/z: calcd for $C_{12}H_{10}NaO_2^+$: 209.0573 $(M + Na)^+$, found: 209.0578.

Methyl 4-acetylbenzoate 3g. 63.4 mg, 89% (for **1g**); 67.7 mg, 95% (for **4d**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.50, 166.19, 140.21, 133.87, 129.80, 128.17, 52.43, 26.84. HRMS (ESI-TOF) m/z: calcd for $C_{10}H_{10}NaO_3^+$: 201.0522 $(M + Na)^+$, found: 201.0519.

Methyl 3-acetylbenzoate 3h. 61.2 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.21 (d, J = 7.7 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 3.94 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.23, 166.28, 137.26, 133.88, 132.28, 130.66, 129.53, 128.84, 52.38, 26.68. HRMS (ESI-TOF) m/z: calcd for $C_{10}H_{10}NaO_3^+$: 201.0522 $(M + Na)^+$, found: 201.0523.

Methyl 2-nitrobenzoate 3io. 59.4 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.8, 1.0 Hz, 1H), 7.73 (dd, J = 7.5, 1.5 Hz, 1H), 7.70–7.59 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.76, 148.12, 132.86, 131.73, 129.74, 127.39, 123.80, 53.14. HRMS (ESI-TOF) m/z: calcd for $C_8H_7NNaO_4^+$: 204.0267 $(M + Na)^+$, found: 204.0273.

Methyl 3-nitrobenzoate 3im. 62.3 mg, 86% (for **1im**); 61.6 mg, 85% (for **4c**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.39 (d, J = 7.1 Hz, 1H), 8.35 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.85, 148.18, 135.18, 131.78, 129.58, 127.30, 124.47, 52.71. HRMS (ESI-TOF) m/z: calcd for $C_8H_7NNaO_4^+$: 204.0267 $(M + Na)^+$, found: 204.0265.

Methyl 4-nitrobenzoate 3ip. 60.1 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16, 150.50, 135.47, 130.69, 123.52, 52.81. HRMS (ESI-TOF) m/z: calcd for $C_8H_7NNaO_4^+$: 204.0267 $(M + Na)^+$, found: 204.0277.

Dimethyl phthalate 3jo. 39.6 mg, 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 5.7, 3.3 Hz, 2H), 7.52 (dd, J = 5.7, 3.3 Hz, 2H), 3.89 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.95, 131.81, 131.02, 128.76, 52.53. HRMS (ESI-TOF) m/z: calcd for $C_{10}H_{10}NaO_4^+$: 217.0471 $(M + Na)^+$, found: 217.0475.

Dimethyl isophthalate 3jm. 68.3 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.21 (dd, J = 7.8, 1.6 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 3.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 133.74, 130.65, 130.53, 128.57, 52.30. HRMS (ESI-TOF) m/z: calcd for $C_{10}H_{10}NaO_4^+$: 217.0471 $(M + Na)^+$, found: 217.0473.

Dimethyl terephthalate 3jp. 73.7 mg, 95% (for **1jp**); 25.6 mg, 66% (for 1,4-diiodobenzene); 76.8 mg, 99% (for **4e**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 4H), 3.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.29, 133.90, 129.54, 52.42. HRMS (ESI-TOF) m/z: calcd for $C_{10}H_{10}NaO_4^+$: 217.0471 $(M + Na)^+$, found: 217.0469.

Methyl 2-fluorobenzoate 3ko. 47.4 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (td, J = 7.6, 1.6 Hz, 1H), 7.53–7.46 (m, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.15–7.09 (m, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.80 (d, J = 3.6 Hz), 161.82 (d, J = 259.8 Hz), 134.39 (d, J = 9.0 Hz), 132.02, 123.85 (d, J = 3.9 Hz), 118.52 (d, J = 9.6 Hz), 116.86 (d, J = 22.4 Hz), 52.19. HRMS (ESI-TOF) m/z: calcd for $C_8H_7FNaO_2^+$: 177.0322 $(M + Na)^+$, found: 177.0323.

Methyl 3-fluorobenzoate 3km. 49.3 mg, 80% (for **1km**); 60.4 mg, 98% (for **4b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 1H), 7.75–7.69 (m, 1H), 7.45–7.37 (m, 1H), 7.29–7.22 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.95 (d, J = 2.7 Hz), 162.52 (d, J = 246.9 Hz), 132.28 (d, J = 7.6 Hz), 129.97 (d, J = 7.8 Hz), 125.28 (d, J = 3.1 Hz), 119.96 (d, J = 21.2 Hz), 116.47 (d, J = 23.1 Hz), 52.35. HRMS (ESI-TOF) m/z: calcd for $C_8H_7FNaO_2^+$: 177.0322 $(M + Na)^+$, found: 177.0318.

Methyl 4-fluorobenzoate 3kp. 54.2 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.7, 5.6 Hz, 2H), 7.06 (t, J = 8.6 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.95, 165.61 (d, J = 253.7 Hz), 131.97 (d, J = 9.3 Hz), 126.29 (d, J = 2.9 Hz), 115.34 (d, J = 22.0 Hz), 51.99. HRMS (ESI-TOF) m/z: calcd for $C_8H_7FNaO_2^+$: 177.0322 $(M + Na)^+$, found: 177.0319.

Methyl 2-chlorobenzoate 3lo. 57.1 mg, 84% (for **1lo**); 42.8 mg, 63% (for **4g**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.7, 1.3 Hz, 1H), 7.46–7.37 (m, 2H), 7.33–7.27 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.06, 133.58, 132.46, 131.29, 130.97, 129.97, 126.48, 52.33. HRMS (ESI-TOF) m/z: calcd for $C_8H_7ClNaO_2^+$: 193.0027 $(M + Na)^+$, found: 193.0029.

Methyl 3-chlorobenzoate 3lm. 59.8 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.1 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.80, 134.44, 132.87, 131.79, 129.62, 129.60, 127.63, 52.32. HRMS (ESI-TOF) m/z: calcd for $C_8H_7ClNaO_2^+$: 193.0027 $(M + Na)^+$, found: 193.0025.

Methyl 4-chlorobenzoate 3lp. 59.8 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.98, 139.16, 130.80, 128.52, 128.42, 52.06. HRMS (ESI-TOF) m/z: calcd for $C_8H_7ClNaO_2^+$: 193.0027 $(M + Na)^+$, found: 193.0028.

Methyl 2-bromobenzoate 3mo. 77.4 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.5, 1.9 Hz, 1H), 7.63 (dd, J = 7.7, 1.2 Hz, 1H), 7.37–7.27 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.48, 134.20, 132.44, 132.00, 131.16, 127.03, 121.50, 52.33. HRMS (ESI-TOF) m/z: calcd for $C_8H_7BrNaO_2^+$: 236.9522 $(M + Na)^+$, found: 236.9523.

Methyl 3-bromobenzoate 3mm. 78.3 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 135.82, 132.56, 132.01, 129.90, 128.11, 122.41, 52.37. HRMS (ESI-TOF) m/z: calcd for $C_8H_7BrNaO_2^+$: 236.9522 $(M + Na)^+$, found: 236.9519.

Methyl 4-bromobenzoate 3mp. 77.6 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.36, 131.70, 131.10, 129.02, 128.02, 52.28. HRMS (ESI-TOF) m/z: calcd for $C_8H_7BrNaO_2^+$: 236.9522 $(M + Na)^+$, found: 236.9523.

Methyl 2-methylbenzoate 3no. 52.8 mg, 88% (for **1no**); 45.0 mg, 75% (for **4ho**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.4 Hz, 1H), 7.40 (t, J = 7.1 Hz, 1H), 7.26–7.22 (m, 2H), 3.89 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.08, 140.15, 131.93, 131.65, 130.53, 129.53, 125.66, 51.78, 21.69. HRMS (ESI-TOF) m/z: calcd for $C_9H_{10}NaO_2^+$: 173.0573 $(M + Na)^+$, found: 173.0575.

Methyl 3-methylbenzoate 3nm. 57.6 mg, 96% (for **1nm**); 58.8 mg, 98% (for **4hm**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 3.91 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26, 138.10, 133.63, 130.08, 130.04, 128.21, 126.66, 52.00, 21.21. HRMS (ESI-TOF) m/z: calcd for $C_9H_{10}NaO_2^+$: 173.0573 $(M + Na)^+$, found: 173.0569.

Methyl 4-methylbenzoate 3np. 58.8 mg, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.18, 143.53, 129.56, 129.04, 127.39, 51.91, 21.61. HRMS (ESI-TOF) m/z: calcd for $C_9H_{10}NaO_2^+$: 173.0573 $(M + Na)^+$, found: 173.0572.

Methyl 2-(trifluoromethyl)benzoate 3oo. 43.2 mg, 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.70 (m, 2H), 7.66–7.54 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.25, 131.69, 131.14, 131.02, 130.04, 128.73 (q, J = 32.5 Hz), 126.64 (q, J = 5.4 Hz), 123.31 (q, J = 273.3 Hz), 52.77. HRMS (ESI-TOF) m/z: calcd for $C_9H_7F_3NaO_2^+$: 227.0290 $(M + Na)^+$, found: 227.0286.

Methyl 3-(trifluoromethyl)benzoate 3om. 47.3 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.75, 132.77, 131.04 (q, J = 32.9 Hz), 130.97, 129.42 (q, J = 3.5 Hz), 129.03, 126.51 (q, J = 3.9 Hz), 123.64 (q, J = 272.4 Hz), 52.48. HRMS (ESI-TOF) m/z: calcd for $C_9H_7F_3NaO_2^+$: 227.0290 $(M + Na)^+$, found: 227.0287.

Methyl 4-(trifluoromethyl)benzoate 3op. 69.4 mg, 85% (for **1op**); 76.7 mg, 94% (for **4f**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.86, 134.41 (q, J = 32.6 Hz), 133.31, 129.96, 125.38 (q, J = 3.7 Hz), 123.61 (q, J = 272.6 Hz), 52.49. HRMS (ESI-TOF) m/z: calcd for $C_9H_7F_3NaO_2^+$: 227.0290 $(M + Na)^+$, found: 227.0293.

Methyl 2-methoxybenzoate 3po. 37.8 mg, 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 7.9, 1.7 Hz, 1H), 7.59–7.30 (m, 1H), 7.07–6.78 (m, 2H), 3.88 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.60, 158.97, 133.40, 131.51, 119.99, 119.89, 111.89, 55.83, 51.86. HRMS (ESI-TOF) m/z: calcd for $C_9H_{10}NaO_3^+$: 189.0522 $(M + Na)^+$, found: 189.0525.

Methyl 3-methoxybenzoate 3pm. 57.8 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.56 (s, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.10 (dd, J = 8.2, 1.8 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.95, 159.51, 131.40, 129.34, 121.94, 119.47, 113.91, 55.38, 52.13. HRMS (ESI-TOF) m/z: calcd for $C_9H_{10}NaO_3^+$: 189.0522 $(M + Na)^+$, found: 189.0522.

Methyl 4-methoxybenzoate 3pp. 55.8 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.80, 163.28, 131.52, 122.53, 113.54, 55.33, 51.77. HRMS (ESI-TOF) m/z: calcd for $C_9H_{10}NaO_3^+$: 189.0522 $(M + Na)^+$, found: 189.0524.

3-Methyleneisobenzofuran-1(3*H*)-one 3q. 41.5 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 4.1 Hz, 2H), 7.62–7.52 (m, 1H), 5.27–5.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.82, 151.79, 138.95, 134.44, 130.43, 125.23, 125.06, 120.57, 91.23. HRMS (ESI-TOF) m/z: calcd for $C_9H_6NaOS_2^+$: 169.0260 $(M + Na)^+$, found: 169.0262.

Methyl thiophene-2-carboxylate 3r. 12.5 mg, 22% (for **1r**); 55.1 mg, 97% (for **4l**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 3.7, 1.2 Hz, 1H), 7.52 (dd, J = 5.0, 1.2 Hz, 1H), 7.06 (dd, J = 5.0, 3.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.56, 133.45, 133.34, 132.25, 127.63, 52.02. HRMS (ESI-TOF) m/z: calcd for $C_6H_6NaO_2S^+$: 164.9981 $(M + Na)^+$, found: 164.9985.

Di(thiophen-2-yl)methanone 3s. 24.8 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 3.7, 1.0 Hz, 2H), 7.69 (dd, J = 4.9, 1.0 Hz, 2H), 7.18 (dd, J = 4.9, 3.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.75, 142.85, 133.48, 133.13, 127.95. HRMS (ESI-TOF) m/z: calcd for $C_9H_6NaOS_2^+$: 216.9752 $(M + Na)^+$, found: 216.9753.

Methyl thiophene-3-carboxylate 3t. 44.3 mg, 78% (for **1t**); 53.4 mg, 94% (for **4m**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 2.9, 0.9 Hz, 1H), 7.50 (dd, J = 5.0, 0.9 Hz, 1H), 7.28 (dd, J = 5.0, 3.1 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.12, 133.42, 132.56, 127.77, 125.92, 51.68. HRMS (ESI-TOF) m/z: calcd for $C_6H_6NaO_2S^+$: 164.9981 $(M + Na)^+$, found: 164.9983.

Methyl picolinate 3u. 15.4 mg, 28% (for **4n**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 4.0 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.84 (ddd, J = 7.8, 7.8, 1.7 Hz, 1H), 7.48 (ddd, J = 7.6, 4.7, 1.0 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.68,

149.78, 147.89, 137.03, 126.94, 125.12, 52.88. HRMS (ESI-TOF) *m*/*z*: calcd for $C_7H_7NNaO_2^+$: 160.0369 $(M + Na)^+$, found: 160.0366.

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Notes and references

1 (*a*) S. Patai, *Carboxylic Acids and Esters (1969)*, Wiley-Blackwell, Chichester, 1969; (*b*) M. Mori, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. E. Negishi, Wiley-Interscience, New York, 2002, pp. 2663–2682; (*c*) J. E. Robbers, H. Otsuka, H. G. Floss, E. V. Arnold and J. Clardy, *J. Org. Chem.*, 1980, **45**, 1117; (*d*) L. J. Gooen, N. Rodrguez and K. Gooen, *Angew. Chem., Int. Ed.*, 2008, **47**, 3100; (*e*) J. R. Dunetz, J. Magano and G. A. Weisenburger, *Org. Process Res. Dev.*, 2016, **20**, 140; (*f*) Y. Ikeda, A. Murakami and H. Ohigashi, *Mol. Nutr. Food Res.*, 2008, **52**, 26; (*g*) S. E. David, P. Timmins and B. R. Conway, *Drug Dev. Ind. Pharm.*, 2012, **38**, 93; (*h*) S. Urwyler, P. Floersheim, B. L. Roy and M. Koller, *J. Med. Chem.*, 2009, **52**, 5093.

2 (*a*) M. A. Ogliaruso and J. F. Wolfe, *Synthesis of Carboxylic Acids, Esters and Their Derivatives (1991)*, Wiley-Blackwell, Chichester, 1991; (*b*) E. A. Quadrelli, G. Centi, J.-L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194; (*c*) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312; (*d*) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365; (*e*) B. Yu, Z.-F. Diao, C.-X. Guo and L.-N. He, *J. CO2 Util.*, 2013, **1**, 60; (*f*) I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384; (*g*) Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933.

3 (*a*) L. Kollr, *Modern Carbonylation Methods*, Wiley-VCH, Weinheim, 2008; (*b*) M. Beller, *Catalytic carbonylation reactions*, Springer, Berlin, 2006; (*c*) M. Beller and X.-F. Wu, *Transition Metal Catalyzed Carbonylation Reactions*, Springer, Berlin, 2013; (*d*) M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.*, 1995, **104**, 17; (*e*) P. Gehrtz, V. Hirschbeck, B. Ciszek and I. Fleischer, *Synthesis*, 2016, 1573; (*f*) Z. Zhang, Y. Zhang and J. Wang, *ACS Catal.*, 2011, **1**, 1621; (*g*) C. Torborg and M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 3027; (*h*) A. Brennfhrer, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2009, **48**, 4114; (*i*) Q. Liu, H. Zhang and A. Lei, *Angew. Chem., Int. Ed.*, 2011, **50**, 10788; (*j*) J. Magano and J. R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177; (*k*) C. F. J. Barnard, *Organometallics*, 2008, **27**, 5402.

4 (*a*) A. Schoenberg and R. F. Heck, *J. Org. Chem.*, 1974, **39**, 3327; (*b*) A. Schoenberg, I. Bartoletti and R. F. Heck, *J. Org. Chem.*, 1974, **39**, 3318.

5 (*a*) T. Morimoto and K. Kakiuchi, *Angew. Chem., Int. Ed.*, 2004, **43**, 5580; (*b*) L. Wu, Q. Liu, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2014, **53**, 6310; (*c*) P. Gautam and B. M. Bhanage, *Catal. Sci. Technol.*, 2015, **5**, 4663.

6 P. Hermange, T. M. Ggsig, A. T. Lindhardt, R. H. Taaning and T. Skrydstrup, *Org. Lett.*, 2011, **13**, 2444.

7 S. D. Friis, R. H. Taaning, A. T. Lindhardt and T. Skrydstrup, *J. Am. Chem. Soc.*, 2011, **133**, 18114.

8 P. Hermange, A. T. Lindhardt, R. H. Taaning, K. Bjerglund, D. Lupp and T. Skrydstrup, *J. Am. Chem. Soc.*, 2011, **133**, 6061.

9 (*a*) T. Ueda, H. Konishi and K. Manabe, *Org. Lett.*, 2013, **15**, 5370; (*b*) T. Ueda, H. Konishi and K. Manabe, *Angew. Chem., Int. Ed.*, 2013, **52**, 8611.

10 (*a*) H. Konishi and K. Manabe, *Synlett*, 2014, 1971; (*b*) C. Brancour, T. Fukuyama, Y. Mukai, T. Skrydstrup and I. Ryu, *Org. Lett.*, 2013, **15**, 2794; (*c*) C.-L. Li, X. Qi and X.-F. Wu, *ChemistrySelect*, 2016, **1**, 1702; (*d*) J. Hou, J.-H. Xie and Q.-L. Zhou, *Angew. Chem., Int. Ed.*, 2015, **54**, 6302; (*e*) S. Korsager, R. H. Taaning and T. Skrydstrup, *J. Am. Chem. Soc.*, 2013, **135**, 2891; (*f*) D.-S. Kim, W.-J. Park, C.-H. Lee and C.-H. Jun, *J. Org. Chem.*, 2014, **79**, 12191; (*g*) C. Zhu, J. Takaya and N. Iwasawa, *Org. Lett.*, 2015, **17**, 1814; (*h*) T. Ueda, H. Konishi and K. Manabe, *Org. Lett.*, 2012, **14**, 5370; (*i*) T. Fujihara, T. Hosoki, Y. Katafuchi, T. Iwai, J. Terao and Y. Tsuji, *Chem. Commun.*, 2012, **48**, 8012; (*j*) H. Li, H. Neumann, M. Beller and X.-F. Wu, *Angew. Chem., Int. Ed.*, 2014, **53**, 3183; (*k*) W. Ren, W. Chang, Y. Wang, J. Li and Y. Shi, *Org. Lett.*, 2015, **17**, 3544; (*l*) S. Ding and N. Jiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 9226; (*m*) X. Wu, Y. Zhao and H. Ge, *J. Am. Chem. Soc.*, 2015, **137**, 4924; (*n*) J. Chen, J.-B. Feng, K. Natte and X.-F. Wu, *Chem. – Eur. J.*, 2015, **21**, 16370; (*o*) Y. Wan, M. Alterman, M. Larhed and A. Hallberg, *J. Org. Chem.*, 2002, **67**, 6232.

11 (*a*) P. Caldirola, R. Chowdhury, A. M. Johansson and U. Hacksell, *Organometallics*, 1995, **14**, 3897; (*b*) J.-J. Brunet and M. Taillefer, *J. Organomet. Chem.*, 1990, **384**, 193; (*c*) A. WiÈ©ckowska, R. Fransson, L. R. Odell and M. Larhed, *J. Org. Chem.*, 2011, **76**, 978; (*d*) R. Nakaya, H. Yorimitsu and K. Oshima, *Chem. Lett.*, 2011, **40**, 904; (*e*) N.-F. K. Kaiser, A. Hallberg and M. Larhed, *J. Comb. Chem.*, 2002, **4**, 109; (*f*) L. Odell, F. Russo and M. Larhed, *Synlett*, 2012, 685; (*g*) N. L. Bauld, *Tetrahedron Lett.*, 1963, **4**, 1841; (*h*) E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, 1969, **91**, 1233.

12 (*a*) K. Natte, A. Dumrath, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2014, **53**, 10090; (*b*) F. Y. Kwong, H. W. Lee, L. Qiu, W. H. Lam, Y.-M. Li, H. L. Kwong and A. S. C. Chan, *Adv. Synth. Catal.*, 2005, **347**, 1750; (*c*) T. Morimoto, K. Fuji, K. Tsutsumi and K. Kakiuchi, *J. Am. Chem. Soc.*, 2002, **124**, 3806; (*d*) Q. Liu, L. Wu, R. Jackstell and M. Beller, *ChemCatChem*, 2014, **6**, 2805;

(*e*) K. H. Park and Y. K. Chung, *Adv. Synth. Catal.*, 2005, **347**, 854; (*f*) T. Shibata, N. Toshida, M. Yamasaki, S. Maekawa and K. Takagi, *Tetrahedron*, 2005, **61**, 9974; (*g*) W. Li and X.-F. Wu, *J. Org. Chem.*, 2014, **79**, 10410.

13 (*a*) J. Hine, *J. Am. Chem. Soc.*, 1950, **72**, 2438; (*b*) Z. Li and L. Wang, *Adv. Synth. Catal.*, 2015, **357**, 3469; (*c*) V. V. Grushin and H. Alper, *Organometallics*, 1993, **12**, 3846; (*d*) X. Liu, B. Li and Z. Gu, *J. Org. Chem.*, 2015, **80**, 7547; (*e*) S. N. Gockel and K. L. Hull, *Org. Lett.*, 2015, **17**, 3236.

14 (*a*) J. H. Park, Y. Cho and Y. K. Chung, *Angew. Chem., Int. Ed.*, 2010, **49**, 5138; (*b*) H.-S. Park, D.-S. Kim and C.-H. Jun, *ACS Catal.*, 2015, **5**, 397; (*c*) S. H. Christensen, E. P. K. Olsen, J. Rosenbaum and R. Madsen, *Org. Biomol. Chem.*, 2015, **13**, 938.

15 K. Ikeda, T. Morimoto and K. Kakiuchi, *J. Org. Chem.*, 2010, **75**, 6279.

16 (*a*) R. Shang, Y. Fu, J.-B. Li, S.-L. Zhang, Q.-X. Guo and L. Liu, *J. Am. Chem. Soc.*, 2009, **131**, 5738; (*b*) M. Li, C. Wang, P. Fang and H. Ge, *Chem. Commun.*, 2011, **47**, 6587; (*c*) J. Miao, P. Fang, S. Jagdeep and H. Ge, *Org. Chem. Front.*, 2016, **3**, 243; (*d*) Z.-Y. Li and G.-W. Wang, *Org. Lett.*, 2015, **17**, 4866.

17 S. V. F. Hansen and T. Ulven, *Org. Lett.*, 2015, **17**, 2832.

18 M. Markovič, P. Lopatka, P. Koóš and T. Gracza, *Org. Lett.*, 2015, **17**, 5618.

19 A. K. Shil, S. Kumar, C. B. Reddy, S. Dadhwal, V. Thakur and P. Das, *Org. Lett.*, 2015, **17**, 5352.

20 (*a*) E. Negishi and J. M. Tour, *Tetrahedron Lett.*, 1986, **27**, 4869; (*b*) P. G. Ciattini, G. Mastropietro, E. Morera and G. Ortar, *Tetrahedron Lett.*, 1993, **34**, 3763; (*c*) E. Negishi, H. Makabe, I. Shimoyama, G. Wu and Y. Zhang, *Tetrahedron*, 1998, **54**, 1095.

21 G. Ortar, A. Schiano Moriello, E. Morera, M. Nalli, V. Di Marzo and L. De Petrocellis, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 5614.

22 (*a*) H. Sugimoto, I. Kawata, H. Taniguchi and Y. Fujiwara, *J. Organomet. Chem.*, 1984, **266**, c44; (*b*) C. S. Yeung and V. M. Dong, *J. Am. Chem. Soc.*, 2008, **130**, 7826; (*c*) A. Correa and R. Martín, *J. Am. Chem. Soc.*, 2009, **131**, 15974; (*d*) H. Tran-Vu and O. Daugulis, *ACS Catal.*, 2013, **3**, 2417; (*e*) T. Fujihara, K. Nogi, T. Xu, J. Terao and Y. Tsuji, *J. Am. Chem. Soc.*, 2012, **134**, 9106.

23 (*a*) S. Cacchi, G. Fabrizi and A. Goggiamani, *Org. Lett.*, 2003, **5**, 4269; (*b*) A. V. Gadakh, D. Chikanna, S. S. Rindhe and B. K. Karale, *Synth. Commun.*, 2012, **42**, 658; (*c*) H. G. Khorana, *Chem. Rev.*, 1953, **53**, 145.

