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PAPER

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

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

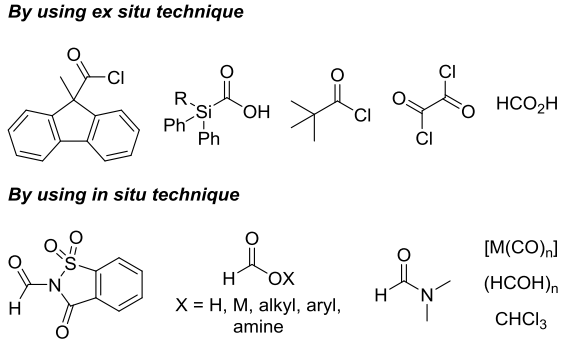
An efficient palladium-catalyzed hydroxycarbonylation reaction of arylhalides using oxalic acid as CO source has been developed. The reaction features high safety, low catalyst loading, and broad substrate scope, and provides a safe and tractable approach to access a variety of aromatic carboxylic acid 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 bearing 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 is no doubt related to the highly toxic, colorless, flavorless, explosible properties of carbon monoxide, and in most cases specialized high-pressure equipment are 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 their derivatives can be treated as CO producers.[10] Metal carbonyl complexes,[11] 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 their derivatives are inexpensive, nontoxic, and abundant chemicals. Few examples have demonstrated that



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
Homepage: 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] Shanghai Key Laboratory of Chemical Assessment and Sustainability, 1239 Siping Road, Shanghai 200092, P.R. China.
[d] College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, P. R. China

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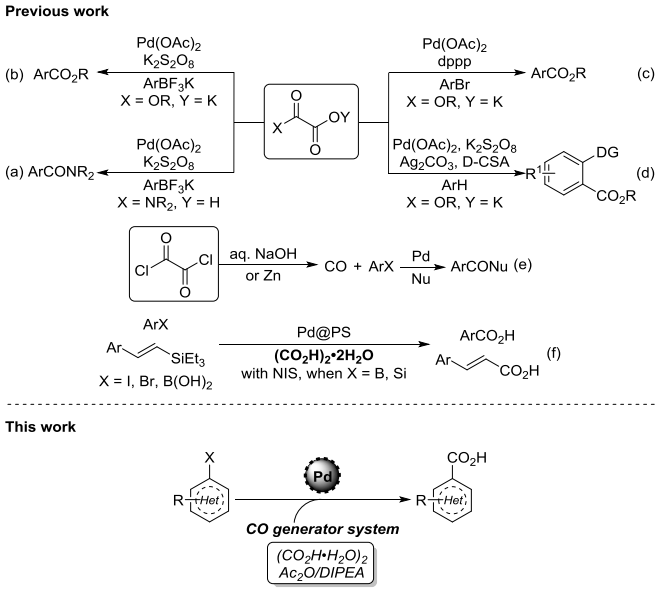


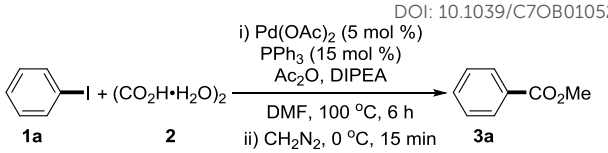
Scheme 2 Examples of using oxalic acid derivatives in carbonylation reactions.

oxalic acid and their derivatives have the potential to be CO surrogates. Liu, Ge, and Gu reported several palladium-catalyzed decarboxylative cross-coupling reactions of potassium oxalate monoesters or oxamic acids with arylhalides, arylborates, and C−H bonds (Scheme 2, a-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 CO gas balloon or two-chamber apparatus still can not be avoided in these two reports. Das and co-workers reported a palladium nanoparticle-catalyzed carboxylation of arylhalides. Despite the novelty of 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 interests. Herein, we present an example of palladium-catalyzed hydroxycarbonylation reaction of arylhalides using oxalic acid as the operable concentrated carbonyl reagent.

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 under 100 ^oC for 6 hours followed by sequential esterification operation

Table 1 Conditions screening.



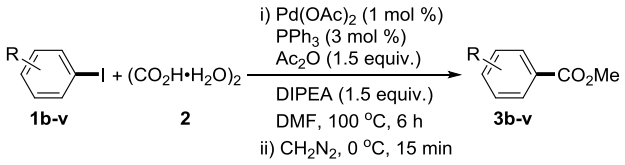
Entry	Variations from condition X[a]	Yield (%)[b]
1	conditions A	94
2	4 h instead of 6 h	85
3	80 ℃ instead of 100 ℃	89
4	conditions B	94
5	conditions C	94
6	1 mol % $Pd(OAc)_2$ was used	94 (90)[c]
7	0.5 mol % $Pd(OAc)_2$ was used	89
8	$Pd(PPh_3)_4$ instead of $Pd(OAc)_2/PPh_3$	92
9	$(CO_2H)_2$ instead 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 $Pd(OAc)_2$	—

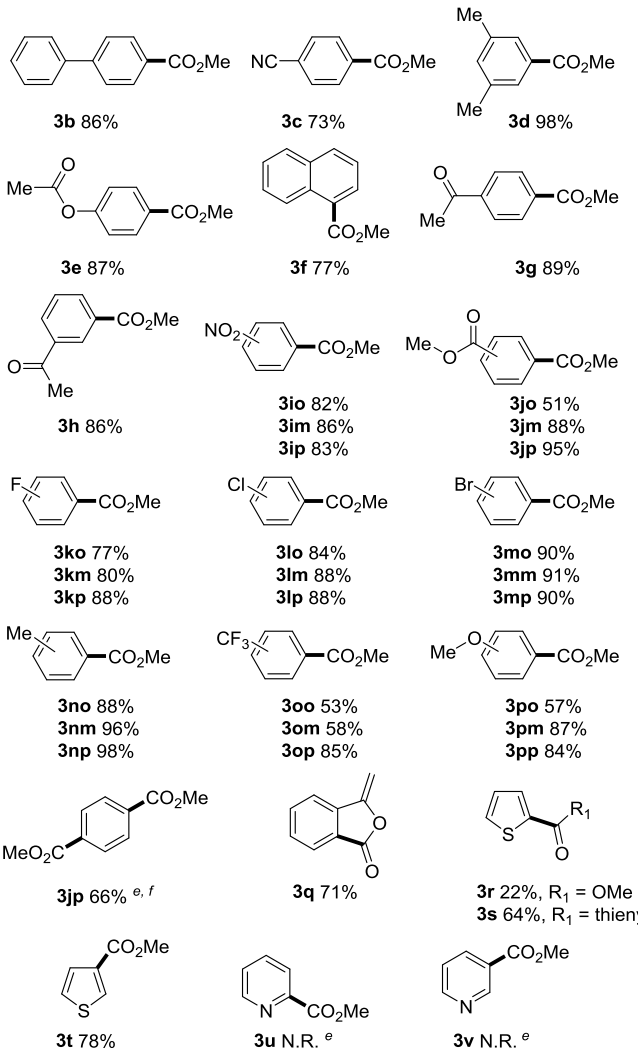
[a] Conditions A: PhI (0.2 mmol), $(CO_2H{\cdot}H_2O)_2$ (3.0 equiv.), Ac_2O (3.0 equiv.), DIPEA (3.0 equiv.). Conditions B: PhI (0.2 mmol), $(CO_2H{\cdot}H_2O)_2$ (2.5 equiv.), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.). Conditions C: PhI (0.4 mmol), $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), Ac_2O (1.5 equiv.), 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.

(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 were summarized in Table 1 (entries 4-5, for details see SI). Based on conditions C, further screening experiments were carried out, and the results illustrated 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 SI). 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 protocol. Gratifyingly, various substituted iodobenzenes (**1b-1v**) underwent the hydroxycarbonylation reaction efficiently, providing aromatic carboxylic acids 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,

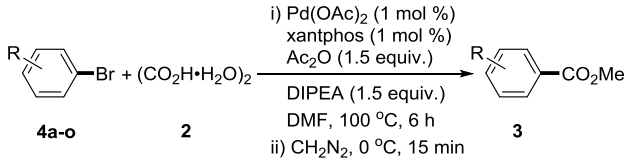
Table 2 Substrate scope of aryliodides.[a, b, c, d]

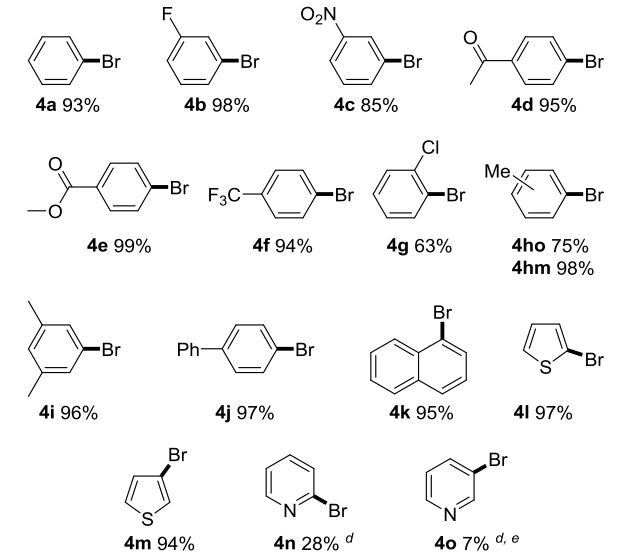




[a] Reaction conditions: Aryliodides (0.4 mmol), $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), $Pd(OAc)_2$ (1 mol %), PPh_3 (3 mol %), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.), DMF (2.0 mL), 100 °C, 6 h. [b] Treated with method A. [c] Isolated yield. [d] 3xo/m/p = ortho/meta/para-position. [e] Treated with method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

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

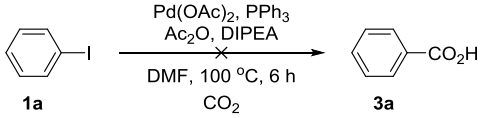




[a] Reaction conditions: Arylbromides (0.4 mmol), $(CO_2H{\cdot}H_2O)_2$ (1.5 equiv.), $Pd(OAc)_2$ (1 mol %), xantphos (1 mol %), Ac_2O (1.5 equiv.), DIPEA (1.5 equiv.), DMF (2.0 mL), 100 °C, 6 h. [b] Treated with method A. [c] Isolated yield. [d] Treated with method B. [e] ^1H NMR yield. xantphos =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

including F (**1k**), Cl (**1l**), and Br (**1m**), survived the reaction conditions. The protocol was applicable for 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, methyl 3-thiophenecarboxylate product (**3t**) was obtained in 78% yield when using 3-iodothiophene as the substrate while 2-iodothiophene gave dithiopheneylketone (**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 SI). Bromobenzene (**4a**) underwent the hydroxycarbonylation reaction under 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**) group 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



Scheme 3 Mechanistic study.

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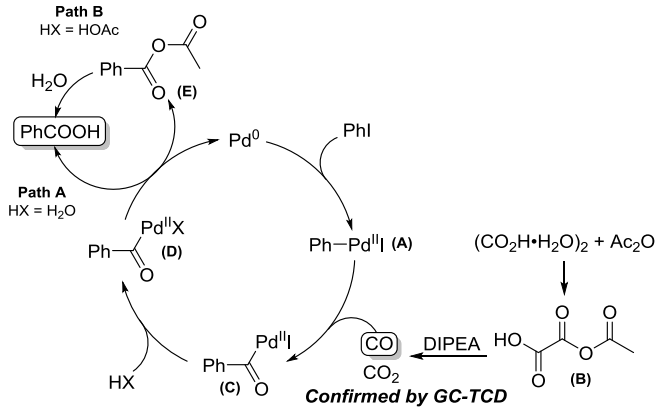

Scheme 4 Plausible mechanism.

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 approximate 1:1 molar ratio after heating the CO generator system in DMF for 1 hour (for details see SI). Secondly, several reports demonstrated that CO_2 was effective carboxylation reagent in Pd-, Ni-, and Cu-catalyzed carboxylation of aryl halides; however, no carboxylated product was detected in our catalytic system under 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 literatures,[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**, 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 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 measured on Bruker MicroTOF II ESI-TOF mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on 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, 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.), DMF (2.0 mL) under air. The tube was quickly sealed with a *Teflon*® high pressure valve. After the reaction mixture was stirred in a preheated oil bath (100 ℃) 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.), DMF (2.0 mL) under 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 ℃) 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 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, CDCl3) 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, CDCl3) 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 (100Z 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(3H)-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, CDCl3) 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, CDCl3) 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, CDCl3) 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, CDCl3) 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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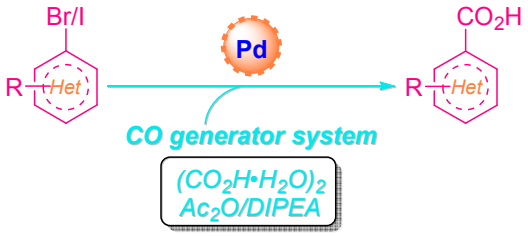
Oxalic acid as the *in situ* carbon monoxide generator in palladium-catalyzed hydroxycarbonylation of arylhalides

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



low catalyst loading 1 mol %
50 examples, yields up to 99%

Oxalic acid as a high efficient, safe and tractable concentrated carbon monoxide surrogate was successfully introduced into the palladium-catalyzed hydroxycarbonylation of arylhalides.