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Supporting Information for

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

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1. General Information.

Method: High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on Bruker ARX400. ¹H NMR spectra were recorded in CDCl₃ referenced to residual CHCl₃ at 7.26 ppm, and ¹³C NMR spectra were referenced to the central peak of CDCl₃ 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.

Materials: Aryl halides, triphenylphosphine, *N*,*N*-diisopropylethylamine, acetic anhydride and oxalic acid dihydrate were purchased from *Adamas-beta*[®], *Aladdin*[®] and *Sinopharm Chemical Reagent Co., Ltd.* separately. Palladium (II) acetate was purchased from *Strem Chemicals, Inc.* Deuterated solvent for NMR analysis was purchased from *Cambridge Isotope Laboratories, Inc.* All the reagents were used directly without further purification.

2. Optimization of Reaction Conditions.

General procedures for the reactions of iodobenzene: A 35 mL sealed tube equipped with a stir bar was charged with oxalic acid dihydrate, palladium (II) acetate, triphenylphosphine, iodobenzene, acetic anhydride, N,N-diisopropylethylamine, N,N-dimethylformamide under air. The tube was quickly sealed with a *Teflon*[®] high pressure valve. After the reaction mixture was stirred in a preheated oil bath for 6 h, it was allowed to cool down to room temperature and diluted with ethyl acetate (10 mL). The reaction mixture was acidified with 2 M hydrochloric acid (5 mL, once) and washed with brine (5 mL, twice). The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The carboxylic acid product was then esterified with diazomethane ether solution. Yields were determined by ¹H NMR analysis of crude products using tetrachloroethane as the internal standard.

| | Pd(0 Ac ₂ O, DIPf | DAc) ₂ , PPh ₃ EA, (COOH•H ₂ | CH ₂ N ₂ | | |
|-------|---------------------------------|--|--------------------------------|-------------------------|------------------------|
| 1a | Air, <mark>ten</mark> | np., time, DMF | | 0 °C, 15 min | 3a 0- |
| Entry | Time (h) ^b | Yield (%) ^d | Entry | Temp. (°C) ^c | Yield (%) ^c |
| 1 | 1 | 70 | 6 | 60 | 82 |
| 2 | 2 | 74 | 7 | 80 | 89 |
| 3 | 4 | 85 | 8 | 100 | 94 |
| 4 | 6 | 94 | 9 | 120 | 94 |
| 5 | 8 | 94 | | | |

Table S1. Screening of the reaction time and temperature.^a

^{*a*} Reaction conditions: Iodobenzene (0.2 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (15 mol %), $(CO_2H\cdot H_2O)_2$ (3.0 equiv.), Ac_2O (3.0 equiv.), DIPEA (3.0 equiv.), DMF (2.0 mL). ^{*b*} 120 °C. ^{*c*} 6 h. ^{*d*} Yields were determined by ¹H NMR analysis of crude products using $C_2H_2Cl_4$ as the internal standard.

| | Pd(OAc) ₂ PPh ₃ (1 Ac ₂ O, DIPEA, | (5 mol %) 5 mol %) (COOH•H ₂ O) ₂ | CH₂N | 2 | | Conditions E |
|----------------|--|---|------------------------------|------------------|---------------------------|---------------------|
| 1a | Air, 100 °C | C, 6 h, DMF | 0 °C, 15 | min 3a | =/ \ 1 | 82% 94% 84% |
| Entry | lodobenzene (mmol) | (COOH•H ₂ O) ₂ (equiv) | Ac ₂ O (equiv) | DIPEA (equiv) | Yield ^a (%) | 61% |
| 1 | 0.20 | 1.00 | 1.00 | 1.00 | 42 | |
| 2 | 0.20 | 1.00 | 2.00 | 2.00 | 61 | 42% |
| 3 | 0.20 | 2.00 | 2.00 | 2.00 | 81 | |
| 4 | 0.20 | 2.00 | 4.00 | 4.00 | 82 | |
| 5 | 0.20 | 3.00 | 2.00 | 2.00 | 94 | All OF TO COST |
| 6 | 0.20 | 2.50 | 2.00 | 2.00 | 94 | |
| 7 ^b | 0.20 | 2.50 | 1.50 | 1.50 | 94 | Conditions C 94% |
| 8 | 0.20 | 2.50 | 1.00 | 1.00 | 64 | 90% |
| 9 | 0.40 | 1.25 | 0.75 | 0.75 | 66 | 660/ |
| 10 | 0.40 | 1.25 | 1.50 | 1.50 | 90 | 00% |
| 11 ° | 0.40 | 1 50 | 1.50 | 1.50 | 94 | |
| 10 | 0.40 | 1.50 | 1.00 | 1.50 | < 2 | |
| 12 | 0.40 | 1.50 | | 1.50 | < Z | |
| 13 | 0.40 | 1.50 | 1.50 | | 12 | |
| 14 | 0.40 | 1.50 | | | 0 | "Ally OF COV |

Table S2. Screening of the component ratios.

^{*a*} Yields were determined by ¹H NMR analysis of crude products using $C_2H_2Cl_4$ as the internal standard. ^{*b*} Conditions B. ^{*c*} Conditions C.

Table S3. Screening of the quantity of Pd catalyst.^a

| | Ac ₂ O, | P <mark>d(OAc)₂, PPh₃</mark> DIPEA, (COOH•H ₂ O) ₂ | Cł | H_2N_2 | | |
|----|--------------------|---|----------|------------------------|----|---|
| 1a | Air | , 100 ^o C, 6 h, DMF | 0 °C, | 15 min | 3a | _ |
| | Entry | Pd(OAc) ₂ / PPh ₃ (1:3, | Pd mol%) | Yield (%) ^b | - | |
| | 1 | 5.0 | | 94 | _ | |
| | 2 | 3.0 | | 94 | | |
| | 3 | 1.0 | | 94 | | |
| | 4 | 0.5 | | 89 | | |
| | 5 | 0.0 | | 0 | _ | |

^{*a*} Reaction conditions: Iodobenzene (0.4 mmol), $(CO_2H \cdot H_2O)_2$ (1.5 equiv.), Ac₂O (1.5 equiv.), DIPEA (1.5 equiv.), DMF (2.0 mL). ^{*b*} Yields were determined by ¹H NMR analysis of crude products using C₂H₂Cl₄ as the internal standard.

Table S4. Screening of the species of Pd catalyst.^a



^{*a*} Reaction conditions: Iodobenzene (0.4 mmol), $(CO_2H \cdot H_2O)_2$ (1.5 equiv.), Ac₂O (1.5 equiv.), DIPEA (1.5 equiv.), DMF (2.0 mL). ^{*b*} Yields were determined by ¹H NMR analysis of crude products using C₂H₂Cl₄ as the internal standard.

General procedures for the reactions of bromobenzene: A 35 mL Schlenk tube equipped with a stir bar was charged with oxalic acid dihydrate, palladium (II) acetate, ligand, bromobenzene, acetic anhydride, *N*,*N*-diisopropylethylamine, *N*,*N*-dimethylformamide under air. The tube was quickly sealed with a *Teflon*[®] high pressure valve, frozen in liquid nitrogen, evacuated and backfilled with N₂ (5 times). After the reaction mixture was stirred in a preheated oil bath for 6 h, it was allowed to cool down to room temperature and diluted with ethyl acetate (10 mL). The reaction mixture was acidified with hydrochloric acid (5 mL, once) and washed with brine (5 mL, twice). The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The carboxylic acid product was then esterified with diazomethane ether solution. Yields were determined by ¹H NMR analysis of crude products using tetrachloroethane as the internal standard.

| ∠—Br — 4a | Pd(OAc) ₂ , Ligand Ac ₂ O, DIPEA, (COOH•H ₂ O) ₂ Atmosphere, 100 °C, 6 h, DMF | | | d •H₂O)₂ ★ - | CH ₂ N ₂ 0 °C, 15 mi | $ \qquad \qquad$ | _ |
|--|---|-------|--------------------|--------------------|---|---|---|
| | | Entry | Ligand | Atmosphere | e Yield (%) ^b | | |
| | | 1 | PPh_3 | Air | 35 | | |
| | | 2 | PPh_3 | N ₂ | 36 | | |
| | | 3 | Pt-Bu ₃ | 3 Air | 5 | | |
| | | 4 | Pt-Bu ₃ | 3 N ₂ | 26 | | |
| | | 5 | xantpho | os Air | 40 | | |
| | | 6 | xantpho | os N ₂ | 96 | | |

Table S5. Conditions screening of the reaction using bromobenzene as the subatrate.^a

^{*a*} Reaction conditions: bromobenzene (0.4 mmol), $(CO_2H \cdot H_2O)_2$ (1.5 equiv.), Pd(OAc)₂ (1 mol %), ligand (3 mol % for PPh₃ and Pt-Bu₃; 1 mol% for xantphos), Ac₂O (1.5 equiv.), DIPEA (1.5

equiv.), DMF (2.0 mL). ^{*b*} Yields were determined by ¹H NMR analysis of crude products using $C_2H_2Cl_4$ as the internal standard.

3. General Procedures for Hydroxycarbonylation.

General procedures for the reactions of aryliodides: A 35 mL sealed tube equipped with a stir bar was charged with oxalic acid dihydrate (1.5 equiv.), palladium (II) acetate (1 mol %), triphenylphosphine (3 mol %), aryliodides (0.4 mmol), acetic anhydride (1.5 equiv.), *N*,*N*-diisopropylethylamine (1.5 equiv.), *N*,*N*-dimethylformamide (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 °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 oxalic acid dehydrate (1.5 equiv.), palladium (II) acetate (1 mol %), xantphos (1 mol %), arylbromides (0.4 mmol), acetic anhydride (1.5 equiv.), *N*,*N*-diisopropylethylamine (1.5 equiv.), *N*,*N*-dimethylformamide (2.0 mL) under air. The tube was quickly sealed with a *Teflon*[®] high pressure valve, frozen in liquid nitrogen, evacuated and backfilled with N₂ (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 ethyl acetate (10 mL), acidified with 2 M hydrochloric acid (5 mL, once), and washed with brine (5 mL, twice). The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The carboxylic acid product was then esterified with diazomethane 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, potassium carbonate (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 ethyl acetate (10 mL) and washed with brine (5 mL, twice). The organic phase was dried over anhydrous sodium sulfate 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.

4. Mechanistic Studies.

$$(CO_2H \bullet H_2O)_2 + Ac_2O + DIPEA \xrightarrow{DMF} CO + CO_2$$

A 35 mL Schlenk flask equipped with a stir bar was charged with oxalic acid dihydrate (0.6 mmol) and sealed with a rubber stopper. The flask was evacuated and backfilled with argon (5 times).

After that, the mixture of acetic anhydride (1.0 equiv.), *N*,*N*-diisopropylethylamine (1.0 equiv.) and *N*,*N*-dimethylformamide (2.0 mL) was injected into the flask via syringe. The tube was quickly moved into a preheated oil bath at 100 °C for 1 hour and allowed to cool down to room temperature. The generated gas from the decomposition of mixed anhydride was characterized by gas chromatogram (GC) analysis (Shimadzu GC-14B) using argon as the carrier gas with a molecular sieve column (5 Å; 30 m \times 0.53 mm) and a thermal conductivity detector (TCD).



| Calibration curve for CO gas | | | | | |
|---|---|--|------------|----------|--|
| volume/µL | peak area 1 | peak area 2 | average pe | eak area | |
| 100 | 40707 | 42868 | 4178 | 7.5 | |
| 200 | 81647 | 82614 | 82130 | 0.5 | |
| 300 | 120268 | 120875 | 12057 | 1.5 | |
| 400 | 157576 | 159556 | 1585 | 66 | |
| 500 | 194301 | 198073 | 1961 | 87 | |
| 600 | 235929 | 233250 | 23458 | 9.5 | |
| 250000 ea 200000 yea 150000 ea 100000 be 50000 0 | y = 384.05 x + R ² = 0.99 8213 41787.5 | 4554.6 999 158566 120571.5 0.5 | 234589.5 | 5 | |
| | 0 100 200 |) 300 400 volume/μL | 500 600 | 700 | |

| Calibration curve for CO2 gas | | | | | | |
|-------------------------------|-------------|-------------|-------------------|--|--|--|
| volume/µL | peak area 1 | peak area 2 | average peak area | | | |
| 100 | 30646 | 29249 | 29947.5 | | | |
| 200 | 59218 | 59748 | 59483 | | | |
| 300 | 84525 | 84173 | 84349 | | | |
| 400 | 116118 | 115872 | 115995 | | | |
| 500 | 144258 | 143310 | 143784 | | | |
| 600 | 173717 | 171807 | 172762 | | | |



The molar ratio of CO/CO_2 in the gas mixture is:

| entry | gas | retention time (min) | peak area | peak height |
|-------|----------------------|---|---------------------------------------|-------------|
| 1 | air | 1.593 | 50259 | 3669 |
| 2 | CO | 2.113 | 92351 | 6256 |
| 3 | $\rm CO_2$ | 11.113 | 60595 | 1027 |
| | $\frac{n_c}{n_{co}}$ | $\frac{V_{co}}{V_{co_2}} = \frac{V_{co}}{V_{co_2}} = \frac{92351 \div 3}{60595 \div 3}$ | $\frac{384.05}{285.32} = \frac{1}{2}$ | <u>13</u> |

5. Characterization of Synthesized Compounds.



Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($\mathbf{R}_f = 0.77$) as the eluent to give the title compound as a colorless oil (49.1 mg, 90% (for **1a**); 50.6 mg, 93% (for **4a**)). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) δ 167.10, 132.88, 130.13, 129.54, 128.32, 52.07. HRMS (ESI-TOF) m/z: calcd for C₈H₈NaO₂⁺: 159.0417 (M + Na)⁺, found: 159.0416.



(3b) Methyl [1,1'-biphenyl]-4-carboxylate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.72$) as the eluent to give the title compound as a white solid (73.0 mg, 86% (for **1b**); 82.3 mg, 97% (for **4j**)). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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 C₁₄H₁₂NaO₂⁺: 235.0730 (M + Na)⁺, found: 235.0733.



(3c) Methyl 4-cyanobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.46$) as the eluent to give the title compound as a light yellow solid (47.0 mg, 73%). ¹H 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). ¹³C 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 C₉H₇NNaO₂⁺: 184.0369 (M + Na)⁺, found: 184.0370.



(3d) Methyl 3,5-dimethylbenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.80$) as the

eluent to give the title compound as a white solid (64.3 mg, 98% (for 1d); 63.0 mg, 96% (for 4i)). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 2H), 7.18 (s, 1H), 3.89 (s, 3H), 2.35 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.40, 137.95, 134.50, 129.96, 127.24, 51.92, 21.08. HRMS (ESI-TOF) m/z: calcd for C₁₀H₁₂NaO₂⁺: 187.0730 (M + Na)⁺, found: 187.0732.

(3e) Methyl 4-acetoxybenzoate

Purified by flash column chromatography on silica gel using PE:EA = 10:1 ($R_f = 0.52$) as the eluent to give the title compound as a white solid (67.5 mg, 87%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 168.82, 166.26, 154.24, 131.12, 127.67, 121.56, 52.16, 21.11. HRMS (ESI-TOF) m/z: calcd for C₁₀H₁₀NaO₄⁺: 217.0471 (M + Na)⁺, found: 217.0469.

(3f) Methyl 1-naphthoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.74$) as the eluent to give the title compound as a white solid (57.3 mg, 77% (for **1f**); 70.7 mg, 95% (for **4k**)). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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 C₁₂H₁₀NaO₂⁺: 209.0573 (M + Na)⁺, found: 209.0578.

(3g) Methyl 4-acetylbenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.34$) as the eluent to give the title compound as a white solid (63.4 mg, 89% (for **1g**); 67.7 mg, 95% (for **4d**)). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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.

(3h) Methyl 3-acetylbenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.36$) as the eluent to give the title compound as a white solid (61.2 mg, 86%). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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 C₁₀H₁₀NaO₃⁺: 201.0522 (M + Na)⁺, found: 201.0523.

(3io) Methyl 2-nitrobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 10:1 ($R_f = 0.40$) as the eluent to give the title compound as a colorless oil (59.4 mg, 82%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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.

(3im) Methyl 3-nitrobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 10:1 ($R_f = 0.49$) as the eluent to give the title compound as a light yellow solid (62.3 mg, 86% (for **1im**); 61.6 mg, 85% (for **4c**)). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) δ 164.85, 148.18, 135.18, 131.78, 129.58, 127.30, 124.47, 52.71. **HRMS** (ESI-TOF) m/z: calcd for C₈H₇NNaO₄⁺: 204.0267 (M + Na)⁺, found: 204.0265.

(3ip) Methyl 4-nitrobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 10:1 ($R_f = 0.55$) as the eluent to give the title compound as a light yellow solid (60.1 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H), 3.98 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) 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.

(3jo) Dimethyl phthalate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.39$) as the eluent to give the title compound as a colorless oil (39.6 mg, 51%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 167.95, 131.81, 131.02, 128.76, 52.53. HRMS (ESI-TOF) m/z: calcd for C₁₀H₁₀NaO₄⁺: 217.0471 (M + Na)⁺, found: 217.0475.

(3jm) Dimethyl isophthalate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.50$) as the eluent to give the title compound as a white solid (68.3 mg, 88%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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.

(3jp) Dimethyl terephthalate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.52$) as the eluent to give the title compound as a white solid (**7**3.7 mg, 95% (for **1jp**); 25.6 mg, 66% (for **1,4-diiodobenzene**); 76.8 mg, 99% (for **4e**)). ¹**H NMR** (400 MHz, CDCl₃) δ 8.10 (s, 4H), 3.94 (s,

6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.29, 133.90, 129.54, 52.42. HRMS (ESI-TOF) m/z: calcd for C₁₀H₁₀NaO₄⁺: 217.0471 (M + Na)⁺, found: 217.0469.

-CO₂Me

(3ko) Methyl 2-fluorobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.75$) as the eluent to give the title compound as a colorless oil (47.4 mg, 77%). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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 C₈H₇FNaO₂⁺: 177.0322 (M + Na)⁺, found: 177.0323.

(3km) Methyl 3-fluorobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.75$) as the eluent to give the title compound as a white solid (49.3 mg, 80% (for 1km); 60.4 mg, 98% (for 4b)). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₈H₂FNaO₂⁺: 177.0322 (M + Na)⁺, found: 177.0318.

(3kp) Methyl 4-fluorobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.76$) as the eluent to give the title compound as a colorless oil (54.2 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (dd, J = 8.7, 5.6 Hz, 2H), 7.06 (t, J = 8.6 Hz, 2H), 3.87 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) 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 C₈H₇FNaO₂⁺: 177.0322 (M + Na)⁺, found: 177.0319.

(3lo) Methyl 2-chlorobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.71$) as the eluent to give the title compound as a colorless oil (57.1 mg, 84% (for **1lo**); 42.8 mg, 63% (for **4g**)). ¹**H NMR** (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 166.06, 133.58, 132.46, 131.29, 130.97, 129.97, 126.48, 52.33. **HRMS** (ESI-TOF) m/z: calcd for C₈H₇ClNaO₂⁺: 193.0027 (M + Na)⁺, found: 193.0029.

(3lm) Methyl 3-chlorobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.69$) as the eluent to give the title compound as a white solid (59.8 mg, 88%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 165.80, 134.44, 132.87, 131.79, 129.62, 129.60, 127.63, 52.32. HRMS (ESI-TOF) m/z: calcd for C₈H₇ClNaO₂⁺: 193.0027 (M + Na)⁺, found: 193.0025.

(3lp) Methyl 4-chlorobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.73$) as the eluent to give the title compound as a white solid (59.8 mg, 88%). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) δ 165.98, 139.16, 130.80, 128.52, 128.42, 52.06. **HRMS** (ESI-TOF) m/z: calcd for C₈H₇ClNaO₂⁺: 193.0027 (M + Na)⁺, found: 193.0028.

(3mo) Methyl 2-bromobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.70$) as the eluent to give the title compound as a colorless oil (77.4 mg, 90%). ¹**H NMR** (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 166.48, 134.20, 132.44, 132.00, 131.16, 127.03, 121.50, 52.33. HRMS (ESI-TOF) m/z: calcd for C₈H₇BrNaO₂⁺: 236.9522 (M + Na)⁺, found: 236.9523.

(3mm) Methyl 3-bromobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.77$) as the eluent to give the title compound as a white solid (78.3 mg, 91%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 165.71, 135.82, 132.56, 132.01, 129.90, 128.11, 122.41, 52.37. HRMS (ESI-TOF) m/z: calcd for C₈H₇BrNaO₂⁺: 236.9522 (M + Na)⁺, found: 236.9519.

(3mp) Methyl 4-bromobenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.79$) as the eluent to give the title compound as a white solid (77.6 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.36, 131.70, 131.10, 129.02, 128.02, 52.28. HRMS (ESI-TOF) m/z: calcd for C₈H₇BrNaO₂⁺: 236.9522 (M + Na)⁺, found: 236.9523.

-CO₂Me

(3no) Methyl 2-methylbenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.74$) as the eluent to give the title compound as a colorless oil (52.8 mg, 88% (for **1no**); 45.0 mg, 75% (for **4ho**)). ¹**H NMR** (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₉H₁₀NaO₂⁺: 173.0573 (M + Na)⁺, found: 173.0575.

(3nm) Methyl 3-methylbenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.75$) as the eluent to give the title compound as a colorless oil (57.6 mg, 96% (for **1nm**); 58.8 mg, 98% (for **4hm**)). ¹**H NMR** (400 MHz, CDCl₃) 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). ¹³C **NMR** (101 MHz, CDCl₃) 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 C₉H₁₀NaO₂⁺: 173.0573 (M + Na)⁺, found: 173.0569.

(3np) Methyl 4-methylbenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.74$) as the eluent to give the title compound as a white solid (58.8 mg, 98%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 167.18, 143.53, 129.56, 129.04, 127.39, 51.91, 21.61. HRMS (ESI-TOF) m/z: calcd for C₉H₁₀NaO₂⁺: 173.0573 (M + Na)⁺, found: 173.0572.

(300) Methyl 2-(trifluoromethyl)benzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.77$) as the eluent to give the title compound as a white solid (43.2 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.70 (m, 2H), 7.66 – 7.54 (m, 2H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) 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 C₉H₇F₃NaO₂⁺: 227.0290 (M + Na)⁺, found: 227.0286.

(3om) Methyl 3-(trifluoromethyl)benzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.73$) as the eluent to give the title compound as a white solid (47.3 mg, 58%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₉H₇F₃NaO₂⁺: 227.0290 (M + Na)⁺, found: 227.0287.

(3op) Methyl 4-(trifluoromethyl)benzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.78$) as the eluent to give the title compound as a light yellow solid (69.4 mg, 85% (for **1op**); 76.7 mg, 94% (for **4f**)). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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 C₉H₇F₃NaO₂⁺: 227.0290 (M + Na)⁺, found: 227.0293.

(3po) Methyl 2-methoxybenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.50$) as the eluent to give the title compound as a colorless oil (37.8 mg, 57%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₉H₁₀NaO₃⁺: 189.0522 (M + Na)⁺, found: 189.0525.

(3pm) Methyl 3-methoxybenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.54$) as the eluent to give the title compound as a white solid (57.8 mg, 87%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₉H₁₀NaO₃⁺: 189.0522 (M + Na)⁺, found: 189.0522.

(3pp) Methyl 4-methoxybenzoate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.60$) as the eluent to give the title compound as a white solid (55.8 mg, 84%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 166.80, 163.28, 131.52, 122.53, 113.54, 55.33, 51.77. HRMS (ESI-TOF) m/z: calcd for C₉H₁₀NaO₃⁺: 189.0522 (M + Na)⁺, found: 189.0524.

(3q) 3-Methyleneisobenzofuran-1(3H)-one

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.90$) as the eluent to give the title compound as a light yellow solid (41.5 mg, 71%). ¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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 C₉H₆NaOS₂⁺: 169.0260 (M + Na)⁺, found: 169.0262.

S CO₂Me

(3r) Methyl thiophene-2-carboxylate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.68$) as the eluent to give the title compound as a light yellow solid (12.5 mg, 22% (for 1r); 55.1 mg, 97% (for 4l)). ¹H 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). ¹³C NMR (101 MHz, CDCl₃) δ 162.56, 133.45, 133.34, 132.25, 127.63, 52.02. HRMS (ESI-TOF) m/z: calcd for C₆H₆NaO₂S⁺: 164.9981 (M + Na)⁺, found: 164.9985.

(3s) Di(thiophen-2-yl)methanone

Purified by flash column chromatography on silica gel using PE:EA = 20:1 (R_f = 0.49) as the eluent to give the title compound as a light yellow solid (24.8 mg, 64%). ¹**H NMR** (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 178.75, 142.85, 133.48, 133.13, 127.95. **HRMS** (ESI-TOF) m/z: calcd for C₉H₆NaOS₂⁺: 216.9752 (M + Na)⁺, found: 216.9753.

(3t) Methyl thiophene-3-carboxylate

Purified by flash column chromatography on silica gel using PE:EA = 20:1 ($R_f = 0.66$) as the eluent to give the title compound as a light yellow oil (44.3 mg, 78% (for 1t); 53.4 mg, 94% (for 4m)). ¹H 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). ¹³C NMR (101 MHz, CDCl₃) δ 163.12, 133.42, 132.56, 127.77, 125.92, 51.68. HRMS (ESI-TOF) m/z: calcd for C₆H₆NaO₂S⁺: 164.9981 (M + Na)⁺, found: 164.9983.

(3u) Methyl picolinate

Purified by flash column chromatography on silica gel using PE:EA = 1:1 (R_f = 0.64) as the eluent to give the title compound as a light yellow oil (15.4 mg, 28% (for **4n**)). ¹**H** NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 165.68, 149.78, 147.89, 137.03, 126.94, 125.12, 52.88. **HRMS** (ESI-TOF) m/z: calcd for C₇H₇NNaO₂⁺: 160.0369 (M + Na)⁺, found: 160.0366.

6. Copies of NMR Spectra.

¹H NMR for 3a Methyl benzoate

¹**H NMR** for **3b** Methyl [1,1'-biphenyl]-4-carboxylate

 1H NMR for 3e Methyl 4-acetoxybenzoate

¹H NMR for 3f Methyl 1-naphthoate

¹H NMR for **3g** Methyl 4-acetylbenzoate

¹H NMR for **3io** Methyl 2-nitrobenzoate

¹H NMR for **3im** Methyl 3-nitrobenzoate

¹H NMR for **3ip** Methyl 4-nitrobenzoate

¹H NMR for **3jo** Dimethyl phthalate

¹H NMR for 3jm Dimethyl isophthalate

 $^1\!H$ NMR for 3jp Dimethyl terephthalate

$^1\!H$ NMR for 3ko Methyl 2-fluorobenzoate

$^1\!H$ NMR for 3km Methyl 3-fluorobenzoate

¹H NMR for 3kp Methyl 4-fluorobenzoate

¹H NMR for 3lo Methyl 2-chlorobenzoate

¹H NMR for 3lm Methyl 3-chlorobenzoate

¹H NMR for 3lp Methyl 4-chlorobenzoate

$^1\!H$ NMR for 3mo Methyl 2-bromobenzoate

¹H NMR for 3mm Methyl 3-bromobenzoate

¹H NMR for 3mp Methyl 4-bromobenzoate

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

¹H NMR for **3no** Methyl 2-methylbenzoate

¹H NMR for 3nm Methyl 3-methylbenzoate

¹H NMR for **3np** Methyl 4-methylbenzoate

¹H NMR for **300** Methyl 2-(trifluoromethyl)benzoate

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

¹H NMR for **3om** Methyl 3-(trifluoromethyl)benzoate

¹H NMR for **3op** Methyl 4-(trifluoromethyl)benzoate

¹H NMR for **3po** Methyl 2-methoxybenzoate

¹H NMR for **3pm** Methyl 3-methoxybenzoate

¹H NMR for **3pp** Methyl 4-methoxybenzoate

 $^1\!H$ NMR for 3q 3-Methyleneisobenzofuran-1(3H)-one

¹H NMR for **3r** Methyl thiophene-2-carboxylate

¹H NMR for 3s Di(thiophen-2-yl)methanone

^{13}C NMR for 3s Di(thiophen-2-yl)methanone

¹H NMR for 3t Methyl thiophene-3-carboxylate

¹H NMR for 3u Methyl picolinate

