Transition-metal-free carbonylation of aryl halides with arylboronic acids by utilizing stoichiometric CHCl$_3$ as the carbon monoxide-precursor

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1. General Information

Reagent Information. All the aryl halides and the arylboronic acids were purchased from Alfa Aesar, Energy Chemical, Beijing InnoChem Science & Technology Co., Ltd., and Accela ChemBio Co., Ltd. and were used as received. Glycol and PEG-400 (bought from Acros, Energy Chemical, and Aladdin) was pre-dried (toluene azeotrope) and deoxygenated. The following reagents were used: Na$_2$CO$_3$ (99.5%, Alfa Aesar), Na$_2$CO$_3$ (99.997%, Alfa Aesar), CsOH·H$_2$O (99%, Energy Chemical), CsOH·H$_2$O (99.95%, Sigma Aldrich), NaI (99%, Alfa Aesar), NaI (99.99%, Acros) and PivOH (99%, Alfa Aesar).

Physical Methods. $^1$H and $^{13}$CNMR spectra of solutions in CDCl$_3$ or CD$_3$COCD$_3$ were recorded on a Bruker Avance 400 instrument. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals (CDCl$_3$: H 7.26 and C 77.0 ppm; CD$_3$COCD$_3$: H 2.05 and C 29.84 ppm). The signals of water were observed at about 1.57 ppm in CDCl$_3$ and 2.84 ppm in CD$_3$COCD$_3$, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet; dt, triplet of doublet; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, $J$, were reported in hertz unit (Hz). Infrared spectra of neat substances were recorded on a BRUKER TENSOR 27 FT-IR spectrometer. HRMS was performed on a Bruker's solarix 94 (ESI-FTICR-MS) mass spectrometer. ICP-AES analysis was measured on a Prodigy (LEEMAN LABS INC.) machine. GC-MS were determined with Agilent 7890-5975C. Column chromatography was performed using silica gel 300-400 mesh (Yantai Jiangyou Silica Gel Co., Ltd., China) as the solid support. No special safety precautions were taken when the reaction was performed in a sealed borosilicate 3.3 glass tube of 3.5 mm wall thickness, 20 mm inside diameter and 3 cm length.

2. General Procedure for transition-metal-free carbonylation of aryl halides with arylboronic acids by utilizing stoichiometric CHCl$_3$ as the CO source

General Procedure A: With no precautions to exclude air or moisture, a 10-ml screw-cap vial equipped with a magnetic stir bar was charged with aryl halide (0.25 mmol), arylboronic acid (0.375 mmol), NaI (0.25 mmol, 37.8 mg), Na$_2$CO$_3$ (0.5 mmol, 53.3 mg), CsOH·H$_2$O (1.25 mmol, 212.0 mg), CHCl$_3$ (0.75
mmol, 61 µL), PivOH (0.1875 mmol, 21 µL), and Glycol (2.0 mL). The vial was capped and heated at 120 °C in a heating block for the indicated time. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 100 : 1 to 10 : 1).

**General Procedure B:** With no precautions to exclude air or moisture, a 10-ml screw-cap vial equipped with a magnetic stir bar was charged with aryl halide (0.25 mmol), arylboronic acid (0.375 mmol), NaI (0.25 mmol, 37.8 mg), Na₂CO₃ (0.75 mmol, 80.0 mg), CsOH·H₂O (1.25 mmol, 212.0 mg), CHCl₃ (0.75 mmol, 61 µL), PivOH (0.1875 mmol, 21 µL), and Glycol (2.0 mL). The vial was capped and heated at 120 °C in a heating block for the indicated time. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 100 : 1 to 10 : 1).

**General Procedure C:** With no precautions to exclude air or moisture, a 10-ml screw-cap vial equipped with a magnetic stir bar was charged with aryl halide (0.25 mmol), arylboronic acid (0.375 mmol), NaI (0.25 mmol, 37.8 mg), Na₂CO₃ (1.0 mmol, 106.6 mg), CsOH·H₂O (1.25 mmol, 212.0 mg), CHCl₃ (0.75 mmol, 61 µL), PivOH (0.1875 mmol, 21 µL), and Glycol (2.0 mL). The vial was capped and heated at 120 °C in a heating block for the indicated time. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 100 : 1 to 10 : 1).

**General Procedure D:** With no precautions to exclude air or moisture, a 10-ml screw-cap vial equipped with a magnetic stir bar was charged with aryl halide (0.25 mmol), arylboronic acid (0.375 mmol), NaI (0.25 mmol, 37.8 mg), Na₂CO₃ (0.50 mmol, 53.3 mg), CsOH·H₂O (1.25 mmol, 212.0 mg), CHCl₃
(0.75 mmol, 61 µL), PivOH (0.1875 mmol, 21 µL), and PEG-400 (2.0 mL). The vial was capped and heated at 120 °C in a heating block for the indicated time. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 100 : 1 to 10 : 1).

3. Effect of A Free-Radical Probe

Following general procedure A, a cyclization product, 3-methyl-2,3-dihydrobenzofuran was obtained based on GC-MS analysis and no any carbonylated product was observed.

4. Comparison of catalyst systems

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<th>Reaction system</th>
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<tr>
<td>1</td>
<td>Pd(dba)$_2$/CO</td>
<td>6h</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)$_2$/CHCl$_3$</td>
<td>17</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>FeCl$_3$/CHCl$_3$</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>CHCl$_3$</td>
<td>This work</td>
<td>94</td>
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*Isolated yields after column chromatography are given.

*Entry 1: A 25 mL flask equipped with a magnetic stir bar was charged with 1m (0.25 mmol, 62.8 mg),
2a (0.25 mmol, 31.4 mg), Pd$_2$(dba)$_3$ (0.0025 mmol, 2.3 mg), K$_2$CO$_3$ (0.75 mmol, 105.8 mg), and anisole (2.0 mL) before standard three cycles of evacuation and back-filling with dry and pure carbon monoxide. The mixture was then stirred at 100 °C for 48 h. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel to give the desired product 3ma (40.3 mg, 72%).

**Entry 2**: With no precautions to exclude air or moisture, a 10-ml screw-cap vial equipped with a magnetic stir bar was charged with 1m (0.25 mmol, 62.8 mg), 2a (0.30 mmol, 37.7 mg), Pd(OAc)$_2$ (0.005 mmol, 1.1 mg), DMAP (0.05 mmol, 6.2 mg), KOH (1.5 mmol, 85.9 mg), CHCl$_3$ (0.75 mmol, 61 µL), and toluene (2.0 mL). The vial was capped and heated at 80 °C in a heating block for 48 h. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel to give the desired product 3ma (27.9 mg, 50%).

**Entry 3**: With no precautions to exclude air or moisture, a 10-ml screw-cap vial equipped with a magnetic stir bar was charged with 1m (0.25 mmol, 62.8 mg), 2a (0.375 mmol, 47.1 mg), FeCl$_2$ (0.025 mmol, 3.2 mg), NaI (0.125 mmol, 18.9 mg), Na$_2$CO$_3$ (0.50 mmol, 53.3 mg), CsOH·H$_2$O (1.25 mmol, 212.0 mg), CHCl$_3$ (0.75 mmol, 61 µL), PivOH (0.375 mmol, 42 µL), and PEG-400 (2.0 mL). The vial was capped and heated at 120 °C in a heating block for 48 h. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel to give the desired product 3ma in 6% yield.

**Entry 4**: With no precautions to exclude air or moisture, a 10-ml screw-cap vial equipped with a magnetic stir bar was charged with 1m (0.25 mmol, 62.8 mg), 2a (0.375 mmol, 47.1 mg), NaI (0.25 mmol, 37.8 mg), Na$_2$CO$_3$ (0.75 mmol, 80.0 mg), CsOH·H$_2$O (1.25 mmol, 212.0 mg), CHCl$_3$ (0.75 mmol, 61 µL), PivOH (0.375 mmol, 42 µL), and PEG-400 (2.0 mL). The vial was capped and heated at 120 °C in a heating block for 48 h. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel to give the desired product 3ma.
mmol, 61 µL), PivOH (0.1875 mmol, 21 µL), and Glycol (2.0 mL). The vial was capped and heated at 120 °C in a heating block for 48 h. The vial was capped and heated at 80 °C in a heating block for 48 h. After being allowed to cool to room temperature, the reaction mixture was diluted with 3 mL water and extracted with diethyl ether (3 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel to give the desired product 3ma (52.6 mg, 94%).

5. Analytical Data of Products

Phenyl(4-(trifluoromethyl)phenyl)methanone (3aa): Following general procedure A, 3aa was isolated as a white solid (53.1 mg, 85%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.90 (d, $J = 8.0$ Hz, 2 H), 7.82-7.79 (m, 2 H), 7.76 (d, $J = 8.0$ Hz, 2 H), 7.63 (tt, $J = 7.2$ Hz, 1.0 Hz, 1 H), 7.51 ppm (t, $J = 7.6$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 195.5, 140.7 (d, $J = 1$ Hz), 136.7, 133.7 (q, $J = 32$ Hz), 133.1, 130.12, 130.09 128.5, 125.3 (q, $J = 3$ Hz), 123.7 ppm (q, $J = 271$ Hz); $^{19}$F NMR (400 MHz, CDCl$_3$): δ -63.0 ppm; Mp: 114.2-115.1 °C.

(4-Nitrophenyl)(phenyl)methanone (3ba): Following general procedure A, 3ba was isolated as light yellow solid (48.2 mg, 85%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.34 (d, $J = 8.8$ Hz, 2 H), 7.94 (d, $J = 8.8$ Hz, 2 H), 7.81-7.79 (m, 2 H), 7.66 (t, $J = 7.6$ Hz, 1 H), 7.53 ppm (t, $J = 7.6$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 194.8, 149.8, 142.8, 136.2, 133.5, 130.7, 130.1, 128.7, 123.5 ppm; Mp: 135.3-136.1 °C.
1-(4-Benzoylphenyl)ethanone (3ca): Following general procedure B, 3ca was isolated as light yellow solid (36.4 mg, 65%), known compound; The NMR spectroscopic data agree with those described in ref.\cite{S2}. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J = 8.0$ Hz, 2 H), 7.87 (d, $J = 8.0$ Hz, 2 H), 7.81-7.79 (m, 2 H), 7.63 (t, $J = 7.6$ Hz, 1 H), 7.50 (t, $J = 7.6$ Hz, 2 H), 2.67 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.6, 196.0, 141.2, 139.5, 136.8, 133.0, 130.1, 130.0, 128.5, 128.1, 26.9 ppm; Mp: 79.5-80.7 °C.

![Cl](4-Chlorophenyl)(phenyl)methanone (3da): Following general procedure A, 3da was isolated as a white solid (47.5 mg, 88%), known compound; The NMR spectroscopic data agree with those described in ref.\cite{S1}. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.74 (m, 4 H), 7.61 (tt, $J = 7.2$ Hz, 1.2 Hz, 1 H), 7.51-7.45 ppm (m, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.5, 138.9, 137.2, 135.9, 132.6, 131.4, 129.9, 128.6, 128.4 ppm; Mp: 71.7-73.2 °C.

![F](4-Fluorophenyl)(phenyl)methanone (3ea): Following general procedure A, 3ea was isolated as a light yellow oil (46.5 mg, 93%), known compound; The NMR spectroscopic data agree with those described in ref.\cite{S1}. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85-7.83 (m, 2 H), 7.78-7.76 (m, 2 H), 7.60 (td, $J = 7.2$ Hz, 1.2 Hz, 1 H), 7.49 (t, $J = 8.4$ Hz, 2 H), 7.17 ppm (td, $J = 8.8$ Hz, 1.6 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.3, 165.4 (d, $J = 253$ Hz), 137.5, 133.7 (d, $J = 4$ Hz), 132.7, 132.6 (d, $J = 14$ Hz), 129.9, 128.3, 115.5 ppm (d, $J = 22$ Hz); $^{19}$F NMR (400 MHz, CDCl$_3$): $\delta$ -106.0 ppm.

![F](3-Fluorophenyl)(phenyl)methanone (3fa): Following general procedure A, 3fa was isolated as a yellow oil (46.0 mg, 92%), known compound; The NMR spectroscopic data agree with those described in ref.\cite{S1}. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (dt, $J = 7.6$ Hz, 1.6 Hz 2 H), 7.63-7.56 (m, 2 H), 7.52-7.44 (m, 4 H), 7.29 ppm (tdd, $J = 8.2$ Hz, 2.4 Hz, 0.8 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.3 (d, $J = 2$ Hz), 162.5 (d, $J = 247$ Hz), 139.6 (d, $J = 6$ Hz), 137.0, 132.8, 130.0, 129.9, 128.4, 125.8 (d, $J$
= 3 Hz), 119.4 (d, \( J = 21 \) Hz), 116.7 ppm (d, \( J = 22 \) Hz); \(^{19}\)F NMR (400 MHz, CDCl\(_3\)): \( \delta = -112.0 \) ppm.

(3,4-Dichlorophenyl)(phenyl)methanone (3ga): Following general procedure B, 3ga was isolated as a white solid (56.3 mg, 90%), known compound; The NMR spectroscopic data agree with those described in ref.\(^{[3]}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.89 \) (d, \( J = 2.0 \) Hz, 1 H), 7.78-7.76 (m, 2 H), 7.65-7.61 (m, 2 H), 7.57 (d, \( J = 8.4 \) Hz, 1 H), 7.51 ppm (t, \( J = 7.6 \) Hz, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 194.3, 137.1, 137.0, 136.6, 132.98, 132.96, 131.8, 130.4, 129.9, 129.1, 128.5 \) ppm; Mp: 99.7-100.4 °C.

(2-Chloro-4-fluorophenyl)(phenyl)methanone (3ha): Following general procedure A, 3ha was isolated as a yellow oil (54.4 mg, 93%), known compound; The NMR spectroscopic data agree with those described in ref.\(^{[4]}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.81 \) (dt, \( J = 8.4 \) Hz, 1.6 Hz, 4 H), 7.60 (tt, \( J = 7.2 \) Hz, 1.2 Hz, 2 H), 7.49 ppm (t, \( J = 7.6 \) Hz, 4 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 194.4, 163.3 \) (d, \( J = 252 \) Hz), 136.4, 134.6 (d, \( J = 4 \) Hz), 133.8, 132.9 (d, \( J = 11 \) Hz), 130.9 (d, \( J = 9 \) Hz), 130.0, 128.6, 117.6 (d, \( J = 24 \) Hz), 114.2 ppm (d, \( J = 22 \) Hz); \(^{19}\)F NMR (400 MHz, CDCl\(_3\)): \( \delta = -107.8 \) ppm.

Benzophenone (3ia): Following general procedure A, 3ia was isolated as a white solid (41.4 mg, 91%), known compound; The NMR spectroscopic data agree with those described in ref.\(^{[1]}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.81 \) (dt, \( J = 8.0 \) Hz, 1.6 Hz, 4 H), 7.60 (tt, \( J = 7.2 \) Hz, 1.2 Hz, 2 H), 7.49 ppm (t, \( J = 7.6 \) Hz, 4 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 196.8, 137.5, 132.4, 130.0, 128.2 \) ppm; Mp: 45.8-46.1 °C.
(4-( tert-Butyl)phenyl)(phenyl)methanone (3ja): Following general procedure A, 3ja was isolated as a white solid with low melting point (42.8 mg, 72%), known compound; The NMR spectroscopic data agree with those described in ref.[83]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81-7.75 (m, 4 H), 7.58 (tt, $J = 7.6$ Hz, 1.2 Hz, 1 H), 7.51-7.46 (m, 4 H), 1.37 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.5, 156.2, 137.9, 134.8, 132.2, 130.1, 130.0, 128.2, 125.2, 35.1, 31.1 ppm.

![Phenyl(m-tolyl)methanone (3ka)](image)

Phenyl(m-tolyl)methanone (3ka): Following general procedure A, 3ka was isolated as a yellow oil (42.6 mg, 87%), known compound; The NMR spectroscopic data agree with those described in ref.[81]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81-7.79 (m, 2 H), 7.63-7.57 (m, 3 H), 7.48 (t, $J = 7.6$ Hz, 2 H), 7.41 (d, $J = 7.6$ Hz, 1 H), 7.36 (t, $J = 7.6$ Hz, 1 H), 2.42 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.0, 138.1, 137.7, 137.6, 133.2, 132.3, 130.4, 130.0, 128.2, 128.1, 127.3, 21.3 ppm.

![Phenyl(3,4,5-trimethoxyphenyl)methanone (3la)](image)

Phenyl(3,4,5-trimethoxyphenyl)methanone (3la): Following general procedure B, 3la was isolated as a white solid with low melting point (51.0 mg, 75%), known compound; The NMR spectroscopic data agree with those described in ref.[86]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81-7.78 (m, 2 H), 7.59 (tt, $J = 7.6$ Hz, 1.2 Hz, 1 H), 7.51-7.47 (m, 2 H), 7.06 (s, 2 H), 3.93 (s, 3 H), 3.87 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.8, 152.8, 141.9, 137.7, 132.5, 132.3, 129.8, 128.2, 107.6, 60.9, 56.2 ppm.

![Mesityl(phenyl)methanone (3ma)](image)

Mesityl(phenyl)methanone (3ma): Following general procedure B, 3ma was isolated as a white solid with low melting point (52.6 mg, 94%), known compound; The NMR spectroscopic data agree with those described in ref.[87]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82-7.80 (m, 2 H), 7.58 (tt, $J = 7.6$ Hz, 1.6 Hz, 1 H), 7.44 (t, $J = 8.0$ Hz, 2 H), 6.90 (s, 2 H), 2.34 (s, 3 H), 2.09 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 200.8, 138.4, 137.2, 136.8, 134.1, 133.5, 129.3, 128.7, 128.3, 21.1, 19.3 ppm.
(2-Isopropylphenyl)(phenyl)methanone (3na): Following general procedure B, 3na was isolated as a yellow oil (45.9 mg, 82%), known compound (CAS: 19103-09-4). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.83-7.81 (m, 2 H), 7.59 (tt, $J = 7.2$ Hz, 1.2 Hz, 1 H), 7.48-7.44 (m, 4 H), 7.25-7.20 (m, 2 H), 3.09-2.99 (m, 1 H), 1.19 ppm (d, $J = 6.8$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 199.1, 147.1, 138.3, 137.7, 133.3, 130.1, 128.4, 127.5, 126.0, 125.1, 30.2, 24.1 ppm.

(2-Methoxyphenyl)(phenyl)methanone (3oa): Following general procedure B, 3oa was isolated as a yellow solid with low melting point (42.9 mg, 81%), known compound; The NMR spectroscopic data agree with those described in ref.$^{[S1]}$. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.83-7.80 (m, 2 H), 7.55 (tt, $J = 7.2$ Hz, 1.2 Hz, 1 H), 7.50-7.41 (m, 3 H), 7.36 (dd, $J = 7.6$ Hz, 1.6 Hz, 1 H), 7.04 (t, $J = 7.2$ Hz, 1 H), 7.00 (d, $J = 8.4$ Hz 1 H), 3.73 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 196.5, 157.3, 137.7, 132.9, 131.9, 129.8, 129.6, 128.7, 128.2, 120.4, 111.4, 55.6 ppm.

4-Benzoylbenzoic acid (3pa): Following general procedure C, 3pa was isolated as a light white solid (33.9 mg, 60%), known compound; The NMR spectroscopic data agree with those described in ref.$^{[S1]}$. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.24 (dd, $J = 6.4$ Hz, 2.0 Hz, 2 H), 7.88 (dd, $J = 6.8$ Hz, 2.0 Hz, 2 H), 7.84-7.81(m, 2 H), 7.64(tt, $J = 7.2$ Hz, 1.2 Hz, 1 H), 7.52 ppm (t, $J = 7.6$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 196.0, 170.8, 142.1, 136.7, 133.1, 132.2, 130.14, 130.12, 129.8, 128.5 ppm; Mp: 195.3-196.1 °C.

(3,5-Dimethylisoxazol-4-yl)(phenyl)methanone (3qa): Following general procedure B, 3qa was isolated as a yellow solid (40.7 mg, 81%), known compound; The NMR spectroscopic data agree with
those described in ref.\[S1\]. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.72-7.70 (m, 2 H), 7.61 (tt, \(J = 7.6\) Hz, 1.2 Hz, 1 H), 7.50 (t, \(J = 8.0\) Hz, 2 H), 2.32 (s, 3 H), 2.30 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.4, 172.3, 159.6, 138.3, 133.2, 128.9, 128.7, 116.4, 13.3, 11.3 ppm; Mp: 55.2-56.9 °C.

Phenyl(thiophen-3-yl)methanone (3ra): Following general procedure B, 3ra was isolated as a light yellow oil (31.5 mg, 67%), known compound. The NMR spectroscopic data agree with those described in ref.\[S1\]. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.93 (dd, \(J = 2.8\) Hz, 1.2 Hz, 1 H), 7.86-7.84 (m, 2 H), 7.58 (dd, \(J = 2.8\) Hz, 1.2 Hz, 1 H), 7.55 (dt, \(J = 7.6\) Hz, 1.2 Hz, 1 H), 7.47 (t, \(J = 8.0\) Hz, 2 H); 7.36 ppm (dd, \(J = 5.2\) Hz, 2.8 Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.0, 141.2, 138.5, 134.0, 132.3, 129.3, 128.6, 128.3, 126.2 ppm.

Naphthalen-1-yl(phenyl)methanone (3sa): Following general procedure B, 3sa was isolated as a white solid (46.4 mg, 80%), known compound; The NMR spectroscopic data agree with those described in ref.\[S1\]. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.11 (dd, \(J = 7.6\) Hz, 0.8 Hz, 1 H), 8.01 (d, \(J = 8.0\) Hz, 1 H), 7.93 (dd, \(J = 7.2\) Hz, 2.0 Hz, 1 H), 7.87 (dt, \(J = 8.4\) Hz, 1.2 Hz, 2 H); 7.63-7.45 ppm (m, 7 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.0, 138.2, 136.2, 133.6, 133.2, 131.2, 130.9, 130.4, 128.40, 128.35, 127.8, 127.2, 126.4, 125.6, 124.3 ppm; Mp: 68.3-69.8 °C.

(2,3-Dihydrobenzofuran-5-yl)(4-(trifluoromethyl)phenyl)methanone (3ab): Following general procedure D, 3ab was isolated as a yellow solid (62.1 mg, 85%), known compound (CAS: 1094286-50-6). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.82 (d, \(J = 8.0\) Hz, 2 H), 7.73 (d, \(J = 8.8\) Hz, 3 H), 7.63 (dd, \(J = 8.4\) Hz, 1.2 Hz, 1 H), 6.83 (d, \(J = 8.4\) Hz, 1 H), 4.69 (t, \(J = 8.4\) Hz, 2 H); 3.27 ppm (t, \(J = 8.4\) Hz, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.3, 164.7, 141.8, 133.1 (q, \(J = 32\) Hz), 132.6, 129.7, 129.6, 127.9, 127.4, 125.2 (q, \(J = 4\) Hz), 123.7 (q, \(J = 271\) Hz), 109.0, 72.3, 28.9 ppm; \(^{19}\)F NMR (400 MHz, CDCl\(_3\)): \(\delta\) -62.9 ppm; Mp: 144.9-145.7 °C.
(4-Fluorophenyl)(4-(trifluoromethyl)phenyl)methanone (3ac): Following general procedure A, 3ac was isolated as a white solid (54.3 mg, 81%), known compound; The NMR spectroscopic data agree with those described in ref.[8]. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.88-7.83 (m, 4 H), 7.76 (d, \(J = 8.4\) Hz, 2 H), 7.19 ppm (tt, \(J = 8.4\) Hz, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.1, 165.7 (d, \(J = 254\) Hz), 140.5 (d, \(J = 1\) Hz), 133.8 (q, \(J = 32\) Hz), 132.9 (d, \(J = 3\) Hz), 132.7 (d, \(J = 9\) Hz), 130.0, 125.4 (q, \(J = 4\) Hz), 123.6 (q, \(J = 271\) Hz), 115.8 ppm (d, \(J = 22\) Hz); \(^{19}\)F NMR (400 MHz, CDCl\(_3\)): \(\delta\) -63.0, -104.6 ppm; Mp: 96.0-97.3 °C.

(3-Chloro-4-fluorophenyl)(4-chlorophenyl)methanone (3dd): Following general procedure A, 3dd was isolated as a yellow solid (56.1 mg, 84%), known compound (CAS: 951890-04-3). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.87 (dd, \(J = 7.2\) Hz, 2.0 Hz, 1 H), 7.74-7.67 (m, 3 H), 7.48 (dt, \(J = 8.4\) Hz, 2.0 Hz, 2 H), 7.26 ppm (t, \(J = 8.4\) Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 192.8, 160.8 (d, \(J = 256\) Hz), 139.4, 135.0, 134.2 (d, \(J = 4\) Hz), 132.6 (d, \(J = 1\) Hz), 131.2, 130.2 (d, \(J = 9\) Hz), 128.9, 121.7 (d, \(J = 19\) Hz), 116.7 ppm (d, \(J = 22\) Hz); \(^{19}\)F NMR (400 MHz, CDCl\(_3\)): \(\delta\) -107.8 ppm; Mp: 75.5-76.6 °C.

(4-Chlorophenyl)(3-isopropylphenyl)methanone (3de): Following general procedure A, 3de was isolated as a yellow oil (47.1 mg, 73%), known compound (CAS: 343221-62-5). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.76 (dt, \(J = 8.4\) Hz, 2.0 Hz, 2 H), 7.66 (s, 1 H), 7.55 (dt, \(J = 7.6\) Hz, 1.6 Hz, 1 H), 7.48-7.45 (m, 3 H), 7.40 (t, \(J = 7.6\) Hz, 1 H), 3.03-2.93 (m, 1 H), 1.28 ppm (d, \(J = 7.2\) Hz, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 195.8, 149.3, 138.7, 137.2, 136.0, 131.5, 130.9, 128.6, 128.2, 127.9, 127.7, 34.0, 23.9 ppm.
(4-Chlorophenyl)(3-nitrophenyl)methanone (3df): Following general procedure A, 3df was isolated as a white solid (44.4 mg, 68%), known compound; The NMR spectroscopic data agree with those described in ref.[89]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.59 (t, $J = 2.0$ Hz, 1 H), 8.46 (dq, $J = 8.4$ Hz, 1.2 Hz, 1 H), 8.11 (dt, $J = 7.6$ Hz, 1.2 Hz, 1 H), 7.77-7.70 (m, 3 H), 7.51 ppm (dt, $J = 8.8$ Hz, 2.0 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.0, 148.0, 140.0, 138.6, 135.3, 134.4, 131.4, 129.8, 129.1, 126.9, 124.6 ppm; Mp: 87.5-88.7 °C.

$p$-Tolyl(4-vinylphenyl)methanone (3tg): Following general procedure A, 3tg was isolated as a white solid (38.9 mg, 70%), known compound (CAS: 24993-89-3). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (dd, $J = 6.8$ Hz, 1.6 Hz, 2 H), 7.71 (d, $J = 8.0$ Hz, 2 H), 7.50 (d, $J = 8.0$ Hz, 2 H), 7.28 (d, $J = 8.0$ Hz, 2 H), 6.78 (dd, $J = 17.6$ Hz, 10.8 Hz, 1 H), 5.89 (d, $J = 17.6$ Hz, 1 H), 5.40 (d, $J = 10.8$ Hz, 1 H), 2.44 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.0, 143.1, 141.2, 137.0, 136.0, 134.9, 130.4, 130.2, 128.9, 125.9, 116.4, 21.7 ppm; Mp: 61.4-62.3 °C.

(4-(Hydroxymethyl)phenyl)(p-tolyl)methanone (3th): Following general procedure A, 3th was isolated as a yellow solid (46.9 mg, 83%), known compound; The NMR spectroscopic data agree with those described in ref.[81]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 8.0$ Hz, 2 H), 7.71 (d, $J = 8.4$ Hz, 2 H), 7.47 (d, $J = 8.0$ Hz, 2 H), 7.28 (d, $J = 8.0$ Hz, 2 H), 4.80 (s, 2 H), 2.44 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.2, 145.1, 143.3, 137.1, 134.9, 130.3, 130.2, 129.0, 126.4, 64.7, 21.7 ppm; Mp: 83.6-84.3 °C.

$m$-Tolyl(4-(trifluoromethoxy)phenyl)methanone (3ki): Following general procedure A, 3ki was isolated as a white solid (63.0 mg, 90%), known compound (CAS: 54362-81-1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (dt, $J = 8.8$ Hz, 2.4 Hz, 2 H), 7.61 (s, 1 H), 7.55 (d, $J = 7.2$ Hz, 1 H), 7.42 (d, $J = 7.6$ Hz, 1 H), 7.38 (t, $J = 7.6$ Hz, 1 H), 7.33-7.30 (m, 2 H), 2.43 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$
195.4, 152.0 (d, J = 2 Hz), 138.4, 137.1, 135.9, 133.5, 131.9, 130.3, 128.2, 127.2, 120.3 (q, J = 257 Hz), 120.2, 21.4 ppm; 19F NMR (400 MHz, CDCl3): δ -57.6 ppm; Mp: 56.4-57.8 °C.

**m-Tolyl(o-tolyl)methanone (3kj):** Following general procedure A, 3kj was isolated as a yellow oil (39.4 mg, 75%), known compound; The NMR spectroscopic data agree with those described in ref.[S10].

1H NMR (400 MHz, CDCl3): δ 7.65 (s, 1 H), 7.56 (d, J = 7.6 Hz, 1 H), 7.41-7.23 (m, 6 H), 2.40 (s, 3 H), 2.33 ppm (s, 3 H); 13C NMR (100 MHz, CDCl3): δ 198.9, 138.7, 138.3, 137.7, 136.6, 133.9, 130.9, 130.4, 130.1, 128.4, 128.3, 127.5, 125.1, 21.3, 20.0 ppm.

![m-Tolyl(o-tolyl)methanone](image)

**(2-Fluorophenyl)(m-tolyl)methanone (3kk):** Following general procedure A, 3kk was isolated as a yellow oil (41.2 mg, 77%), known compound (CAS: 726158-58-3). 1H NMR (400 MHz, CDCl3): δ 7.67 (s, 1 H), 7.60 (d, J = 7.6 Hz, 1 H), 7.56-7.50 (m, 2 H), 7.42 (d, J = 7.6 Hz, 1 H), 7.35 (t, J = 7.6 Hz, 1 H), 7.26 (td, J = 7.6 Hz, 0.8 Hz, 1 H), 7.16 (t, J = 8.8 Hz, 1 H), 2.41 ppm (s, 3 H); 13C NMR (100 MHz, CDCl3): δ 193.7, 160.1 (d, J = 251 Hz), 138.3, 137.4, 134.2, 132.9 (d, J = 8 Hz), 130.7 (d, J = 3 Hz), 130.1, 128.3, 127.2 (d, J = 1 Hz), 124.2 (d, J = 3 Hz), 116.2 (d, J = 22 Hz), 100.0, 21.3 ppm; 19F NMR (400 MHz, CDCl3): δ -111.3 ppm.

![2-Fluorophenyl](image)

**OyO**

**m-Tolyloxy(m-tolyl)oxy)methanone (3ol):** Following general procedure A, 3ol was isolated as a yellow oil (47.6 mg, 70%), known compound (CAS: 757961-86-7). 1H NMR (400 MHz, CDCl3): δ 7.47-7.43 (m, 1 H), 7.32 (dd, J = 7.2 Hz, 2.0 Hz, 1 H), 7.02 (td, J = 7.6 Hz, 0.8 Hz, 1 H), 6.98 (d, J = 8.4 Hz, 1 H), 6.96 (d, J = 2.0 Hz, 2 H), 6.65 (t, J = 2.4 Hz, 1 H), 3.80 (s, 6 H), 3.75 ppm (s, 3 H); 13C NMR (100 MHz, CDCl3): δ 196.1, 160.5, 157.2, 139.6, 131.7, 129.3, 128.7, 120.3, 111.4, 107.6, 105.4, 55.6, 55.5 ppm.
(2-Methoxyphenyl)(naphthalen-1-yl)methanone (3om): Following general procedure A, 3om was isolated as a yellow solid (49.8 mg, 76%), known compound; The NMR spectroscopic data agree with those described in ref.[8][11]. 1H NMR (400 MHz, CDCl₃): δ 8.62 (d, J = 8.4 Hz, 1 H), 7.98 (d, J = 8.4 Hz, 1 H), 7.92-7.89 (m, 1 H), 7.61-7.48 (m, 5 H), 7.42 (dd, J = 8.4 Hz, 7.6 Hz, 1 H), 7.04 (td, J = 7.2 Hz, 0.8 Hz, 1 H), 6.97 (d, J = 8.4 Hz, 1 H), 3.61 ppm (s, 3 H); 13C NMR (100 MHz, CDCl₃): δ 197.9, 158.3, 136.7, 133.7, 132.8, 132.2, 130.8, 130.7, 129.9, 129.8, 128.3, 127.6, 126.2, 125.9, 124.3, 120.4, 111.8, 55.6 ppm; Mp: 73.8-74.7 °C.

(4-Chlorophenyl)(3,4,5-trimethoxyphenyl)methanone (3ln): Following general procedure A, 3ln was isolated as a white solid (50.5 mg, 66%), known compound; The NMR spectroscopic data agree with those described in ref.[8][12]. 1H NMR (400 MHz, CD₃COCD₃): δ 7.82 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.09 (s, 2 H), 3.86 (s, 6 H), 3.83 ppm (s, 3 H); 13C NMR (100 MHz, CD₃COCD₃): δ 194.3, 154.0, 143.2, 138.7, 137.3, 133.0, 132.3, 129.4, 108.3, 60.7, 56.5 ppm; Mp: 98.2-99.7 °C.

(3,5-Dichlorophenyl)(mesityl)methanone (3mo): Following general procedure B, 3mo was isolated as a white solid with low melting point (63.5 mg, 87%), known compound (CAS: 1096971-39-9). 1H NMR (400 MHz, CDCl₃): δ 7.64 (d, J = 1.6 Hz, 2 H), 7.56 (t, J = 2.0 Hz, 1 H), 6.91 (s, 2 H), 2.34 (s, 3 H), 2.07 ppm (s, 6 H); 13C NMR (100 MHz, CDCl₃): δ 198.1, 139.8, 139.3, 135.9, 135.3, 134.2, 133.2, 128.6, 127.5, 21.2, 19.4 ppm.
2-(4-(4-Chlorobenzoyl)phenoxy)-2-methylpropanoic acid (3un): Following general procedure C, 3un was isolated as a white solid (57.2 mg, 72%), known compound; The NMR spectroscopic data agree with those described in ref[813]. 1H NMR (400 MHz, CD$_3$COCD$_3$): δ 7.79-7.75 (m, 4 H), 7.58 (dt, J = 8.8 Hz, 2.0 Hz, 2 H), 6.99 (dt, J = 8.8 Hz, 2.4 Hz, 2 H), 1.67 ppm (s, 6 H); 13C NMR (100 MHz, CD$_3$COCD$_3$): δ 194.0, 174.9, 160.7, 138.4, 137.7, 132.6, 132.1, 131.0, 129.3, 118.2, 79.9, 25.6 ppm; Mp: 177.1-178.6 °C.

![Naphthalen-2-yl(3,4,5-trimethoxyphenyl)methanone (3lp):](image)

Naphthalen-2-yl(3,4,5-trimethoxyphenyl)methanone (3lp): Following general procedure B, 3lp was isolated as a white solid (51.5 mg, 64%), known compound; The NMR spectroscopic data agree with those described in ref[809]. 1H NMR (400 MHz, CD$_3$COCD$_3$): δ 8.38 (s, 1 H), 8.11 (d, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 8.02 (d, J = 8.0 Hz, 1 H), 7.92 (dd, J = 8.4 Hz, 2.0 Hz, 1 H), 7.69-7.60 (m, 2 H), 7.18 (s, 2 H), 3.86 (s, 6 H), 3.85 ppm (s, 3 H); 13C NMR (100 MHz, CD$_3$COCD$_3$): δ 195.5, 154.0, 143.0, 136.0, 133.7, 133.3, 132.1, 130.3, 129.14, 129.05, 128.6, 127.7, 126.5, 108.5, 60.7, 56.5 ppm; Mp: 106.4-107.2 °C.

Naphthalen-2-yl(3,4,5-trimethoxyphenyl)methanone (13C-3lp): Following general procedure B, 13C-3lp was isolated as a white solid (51.7 mg, 64%). 1H NMR (400 MHz, CD$_3$COCD$_3$): δ 8.38 (d, J = 3.6 Hz, 1 H), 8.11 (d, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 8.02 (d, J = 8.0 Hz, 1 H), 7.92 (ddd, J = 8.4 Hz, 3.2 Hz, 1.6 Hz, 1 H), 7.69-7.60 (m, 2 H), 7.18 (d, J = 4.0 Hz, 2 H), 3.864 (s, 6 H), 3.855 ppm (s, 3 H); 13C NMR (100 MHz, CD$_3$COCD$_3$): δ 195.5, 154.0 (d, J = 6 Hz), 143.1, 136.0, 135.9 (d, J = 55 Hz), 133.5 (d, J = 56 Hz), 133.3 (d, J = 5 Hz), 132.1 (d, J = 3 Hz), 130.3, 129.2, 129.1 (d, J = 4 Hz), 128.6, 127.7, 126.5 (d, J = 3 Hz), 108.5 (d, J = 3 Hz), 60.7, 56.6 ppm; HRMS (ESI) calcd. for C$_{19}$H$_{18}$O$_4$ [M + H$^+$] m/z 324.1311, found 324.1316; Mp: 106.6-107.5 °C.
6. References


7. Copies of NMR Spectra

$^{1}H$ NMR (400 MHz, CDCl3)

$^{13}C$ NMR (100 MHz, CDCl3)
$^{19}$F NMR (400 MHz, CDCl$_3$)
^H NMR (400 MHz, CDCl_3)

^13C NMR (100 MHz, CDCl_3)
$^{19}F$ NMR (400 MHz, CDCl$_3$)
$^{19}$F NMR (400 MHz, CDCl$_3$)
\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \]

\[ \text{^13C NMR (100 MHz, CDCl}_3 \text{)} \]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (400 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$\text{S33}$

$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{C NMR (100 MHz, CDCl}_3\text{)}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
HNM(400 MHz, CDCl₃)
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}F$ NMR (400 MHz, CDCl$_3$)
$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{^13C NMR (100 MHz, CDCl}_3\text{)}$
$^{19}$F NMR (400 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_{3}$)

$^{13}$C NMR (100 MHz, CDCl$_{3}$)
$^{19}$F NMR (400 MHz, CDCl$_3$)