Transition-Metal-Free, Ambient-Pressure Carbonylative Cross-Coupling Reactions of Aryl Halides with Potassium Aryltrifluoroborates

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Table of Contents

<table>
<thead>
<tr>
<th>Content</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General Information</td>
<td>S3</td>
</tr>
<tr>
<td>2. Products from Transition-Metal-Free Carbonylative Cross Couplings</td>
<td>S3</td>
</tr>
<tr>
<td>3. Effect of Transition Metals on The Carbonylative Cross Coupling</td>
<td>S20</td>
</tr>
<tr>
<td>4. Mechanistic Investigations</td>
<td>S20</td>
</tr>
<tr>
<td>5. References</td>
<td>S23</td>
</tr>
<tr>
<td>6. Copies of NMR Spectra</td>
<td>S25</td>
</tr>
</tbody>
</table>
1. General Information

**Instruments.** $^1$H (400 MHz) and $^{13}$C NMR spectra (100 MHz) of solutions in CDCl$_3$ or DMSO-$d_6$ were recorded on a Bruker Avance 400 NMR spectrometer. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals (CDCl$_3$: $\delta_H$ 7.24 and $\delta_C$ 77.0 ppm; DMSO-$d_6$: $\delta_H$ 2.50 and $\delta_C$ 39.50 ppm). The signals of water were observed at about 1.58 ppm in CDCl$_3$ and 3.33 ppm in DMSO-$d_6$, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, $\ J $, were reported in hertz unit (Hz). HRMS was performed on a Q-TOF mass spectrometer. Infrared spectra of neat substances were recorded on a Thermo Nicolet Corporation GC-FTIR NEXUS670 spectrometer.

**Materials.** All the aryl halides and the Potassium Aryltrifluoroborates were purchased from Alfa Aesar, Adamas, Aladdin, Acros, and Accela ChemBio Co., Ltd. and were used as received. PEG-400 was bought from Aladdin and was pre-dried by using toluene azeotrope.

The following acid and base were used: PivOH (99%, Alfa Aesar); Na$_2$CO$_3$ (99.5%, Alfa Aesar).

2. Products from Transition-Metal-Free Carbonylative Cross Couplings

**General Procedure A:** A 25 mL Schlenk flask was charged with aryl iodide (0.25 mmol), potassium aryl trifluoroborate (0.375 mmol), Na$_2$CO$_3$ (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 100 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was cooled to room temperature, poured into a saturated aqueous NaCl solution (15 mL), and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel.

**General Procedure B:** A 25 mL Schlenk flask was charged with aryl iodide (0.25 mmol), potassium aryl trifluoroborate (0.375 mmol), Na$_2$CO$_3$ (80.0 mg, 0.75 mmol), and PivOH (12.9 mg, 0.125 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 120 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was
cooled to room temperature, and poured into a saturated aqueous NaCl solution (15 mL). The water phase was then acidified to pH 3 with 3 N HCl aqueous solution, and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel.

**General Procedure C**: A 25 mL Schlenk flask was charged with aryl bromide (0.25 mmol), potassium aryl trifluoroborate (0.375 mmol), Na₂CO₃ (53.3 mg, 0.5 mmol), KI (21.0 mg, 0.125 mmol), and PivOH (12.9 mg, 0.125 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 120 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was cooled to room temperature, poured into a saturated aqueous NaCl solution (15 mL), and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel.

**(4-Chlorophenyl)(phenyl)methanone (3aa):** Following general procedure A, 3aa was isolated as a white solid (48 mg, 89%), known compound. The NMR spectroscopic data agree with those described in ref. [S1]. ¹H NMR (400 MHz, CDCl₃): δ 7.77–7.72 (m, 4 H), 7.58 (tt, J = 7.2, 1.2 Hz, 1 H), 7.50–7.43 ppm (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 195.5, 138.9, 137.2, 135.9, 132.6, 131.4, 129.9, 128.6, 128.4 ppm; mp 71.1–71.6 °C.

**(4-Nitrophenyl)(phenyl)methanone (3ba):** Following general procedure A, 3ba was isolated as a light pink solid (49 mg, 86%), known compound. The NMR spectroscopic data agree with those described in ref. [S1]. ¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, J = 8.4 Hz, 2 H), 7.91 (d, J = 8.4 Hz, 2 H), 7.79–7.77 (m, 2 H), 7.65-7.61 (m, 1 H), 7.50 ppm (t, J = 7.6 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 194.8, 149.8, 142.9, 136.3, 133.4, 130.7, 130.1, 128.7, 123.5 ppm; mp 136.7–136.9 °C.
Methyl 4-Benzoylbenzoate (3ca): Following general procedure A, 3ca was isolated as a white solid (47 mg, 78%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.13 (d, $J$ = 8.4 Hz, 2 H), 7.82 (d, $J$ = 8.8 Hz, 2 H), 7.79–7.77 (m, 2 H), 7.60 (tt, $J$ = 7.2 Hz, $J$ = 1.2 Hz, 1 H), 7.50–7.46 (m, 2 H), 3.95 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.0, 166.3, 141.3, 136.9, 133.2, 132.9, 130.1, 129.8, 129.5, 128.4, 52.5 ppm; mp 105.4–106.1 °C.

4-Benzoylbenzoic acid (3da): Following general procedure B, 3da was isolated as a white solid (44 mg, 77%), known compound. The NMR spectroscopic data agree with those described in ref.[S2]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (d, $J$ = 8.4 Hz, 2 H), 7.86 (d, $J$ = 8.4 Hz, 2 H), 7.82–7.79 (m, 2 H), 7.62 (tt, $J$ = 7.2, 1.3 Hz, 1 H), 7.51–7.48 ppm (m, 2 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.4, 166.7, 140.4, 136.5, 134.0, 133.1, 129.7, 129.6, 129.4, 128.7 ppm; mp 193.2–193.5 °C.

2-(4-Benzoylphenoxy)-2-methylpropanoic acid (3ea): Following general procedure B, was isolated as a brown solid (46 mg, 65%), known compound. The NMR spectroscopic data agree with those described in ref.[S19]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.61 (br s, 1 H), 7.77–7.72 (m, 4 H), 7.55 (tt, $J$ = 7.2, 1.2 Hz, 1 H), 7.46–7.42 (m, 2 H), 6.91 (d, $J$ = 8.8 Hz, 2 H), 1.69 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.0, 178.4, 159.0, 137.8, 132.2, 132.18, 131.1, 129.7, 129.6, 129.4, 128.7 ppm; mp 91.6–92.5 °C.

4-Benzoylbenzonitrile (3fa): Following general procedure A except that the reaction temperature is 120 °C, 3fa was isolated as a white solid (45 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S3]. $^1$H NMR
(400 MHz, CDCl$_3$): δ 7.85 (d, J = 8.0 Hz, 2 H), 7.78–7.75 (m, 4 H), 7.62 (tt, J = 7.6, 1.2 Hz, 1 H), 7.51–7.47 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 195.0, 141.2, 136.3, 133.3, 132.1, 130.2, 130.0, 128.6, 118.0, 115.6 ppm; mp 110.8–111.1 °C.

Phe[nyl(4-(trifluoromethyl)phenyl)methanone (3ga): Following general procedure A, 3ga was isolated as a white solid (51 mg, 81%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.87 (d, J = 8.0 Hz, 2 H), 7.80–7.78 (m, 2 H), 7.74 (d, J = 8.0 Hz, 2 H), 7.61 (tt, J = 7.6, 1.6 Hz, 1H), 7.51–7.47 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 195.5, 140.7, 136.7, 133.7 (q, J = 32 Hz), 133.1, 130.11, 130.08, 128.5, 125.3 (q, J = 4 Hz), 123.7 ppm (q, J = 271 Hz); mp 113.4–114.3 °C.

(2,4-Difluorophenyl)(phenyl)methanone (3ha): Following general procedure A, 3ha was isolated as a light yellow oil (38 mg, 70%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.79 (d, J = 8.4 Hz, 2 H), 7.61–7.56 (m, 2 H), 7.49–7.44 (m, 2 H), 7.01–6.96 (m, 1H), 6.92–6.86 ppm (m, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 192.3, 164.9 (dd, J = 253, 12 Hz), 160.9 (dd, J = 254, 12 Hz), 137.4, 133.5, 132.5 (dd, J = 10, 4 Hz), 129.7, 128.5, 123.3 (dd, J = 15, 4 Hz), 111.9 (dd, J = 21, 4 Hz), 104.7 ppm (t, J = 25 Hz).

(4-Fluorophenyl)(phenyl)methanone (3ia): Following general procedure A, 3ia was isolated as a light yellow oil (45 mg, 91%), known compound; The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.84–7.81 (m, 2 H), 7.76–7.74 (m, 2 H), 7.58 (tt, J = 7.2, 1.2 Hz, 1H), 7.49–7.45 (m, 2 H); 7.17–7.11 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 195.3, 165.4 (d, J = 252 Hz), 137.5, 133.8 (d, J = 3 Hz), 132.7, 132.5 (d, J = 15 Hz), 129.9, 128.3, 115.4 ppm (d, J = 22 Hz).
(3-Fluorophenyl)(phenyl)methanone (3ja): Following general procedure A, 3ja was isolated as a light yellow oil (45 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79–7.77 (m, 2 H), 7.61–7.54 (m, 2 H), 7.50–7.43 (m, 4 H), 7.29–7.24 ppm (m, 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).

(3-Fluoro-4-methylphenyl)(phenyl)methanone (3ka): Following general procedure A, 3ka was isolated as a light yellow solid (46 mg, 86%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77–7.75 (m, 2 H), 7.57 (tt, $J = 7.6$, 1.2 Hz, 1 H), 7.48–7.46 (m, 3 H), 7.45 (s, 1 H), 7.29–7.25 (m, 1 H), 2.35 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.2 (d, $J = 2$ Hz), 160.9 (d, $J = 245$ Hz), 137.4, 137.1 (d, $J = 6.5$ Hz), 132.5, 131.3 (d, $J = 4.9$ Hz), 130.2 (d, $J = 17.3$ Hz), 129.9, 128.3, 125.8 (d, $J = 3.4$ Hz), 116.5 (d, $J = 23.3$ Hz), 14.8 ppm (d, $J = 3.5$ Hz); mp 40.0–40.7 °C.

Phenyl(o-tolyl)methanone (3la): Following general procedure A, 3la was isolated as a light yellow oil (42 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80–7.77 (m, 2 H), 7.56 (tt, $J = 7.6$, 1.2 Hz, 1 H), 7.46–7.42 (m, 2 H), 7.38 (td, $J = 7.6$, 1.2 Hz, 1 H), 7.31–7.21 (m, 3 H), 2.32 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.6, 138.6, 137.7, 136.7, 133.1, 131.0, 130.2, 130.1, 128.5, 128.4, 125.2, 19.9 ppm.

Phenyl(m-tolyl)methanone (3ma): Following general procedure A, 3ma was isolated as a light yellow oil (45 mg, 92%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79–
7.77 (m, 2 H), 7.61 (s, 1 H), 7.60–7.54 (m, 2 H), 7.48–7.44 (m, 2 H); 7.39–7.32 (m, 2 H), 2.40 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.0, 138.1, 137.8, 137.6, 133.2, 132.3, 130.4, 130.0, 128.2, 128.1, 127.4, 21.3 ppm.

Phenyl\((p\text{-tolyl})\)methanone (3na): Following general procedure \(A\), 3na was isolated as a white solid with low melting point (46 mg, 94%), known compound. The NMR spectroscopic data agree with those described in ref.\(^{[S1]}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.78–7.75 (m, 2 H), 7.70 (d, \(J = 8.4\) Hz, 2 H), 7.56 (tt, \(J = 7.6, 1.2\) Hz, 1H), 7.48–7.43 (m, 2 H), 7.27–7.25 (m, 2 H), 2.42 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.5, 143.2, 138.0, 134.9, 132.2, 130.3, 129.9, 129.0, 128.2, 21.6 ppm.

\((4\text{-Methoxyphenyl})(\text{phenyl})\)methanone (3oa): Following general procedure \(A\), 3oa was isolated as light white solid (42 mg, 80%), known compound. The NMR spectroscopic data agree with those described in ref.\(^{[S4]}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.81 (d, \(J = 9.2\) Hz, 2 H), 7.75–7.72 (m, 2 H), 7.54 (tt, \(J = 7.2, 1.6\) Hz, 1H), 7.47–7.43 (m, 2 H), 6.94 (d, \(J = 9.2\) Hz, 2 H), 3.86 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 195.5, 163.2, 138.2, 132.5, 131.8, 130.1, 129.7, 128.1,113.5, 55.4 ppm; mp 55.3–56.3 °C.

\((4\text{-Hydroxyphenyl})(\text{phenyl})\)methanone (3pa): Following general procedure \(B\) except that the amounts of Na\(_2\)CO\(_3\) and PivOH are 0.5 mmol and 0.25 mmol, respectively, 3pa was isolated as a light yellow solid (32 mg, 65%), known compound. The NMR spectroscopic data agree with those described in ref.\(^{[S6]}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.77 (d, \(J = 8.8\) Hz, 2 H), 7.74 (dd, \(J = 8.4, 1.2\) Hz, 2 H), 7.56 (tt, \(J = 8.8, 1.6\) Hz, 1H), 7.48–7.44 (m, 2 H), 6.91 (d, \(J = 8.8\) Hz, 2 H), 6.30 ppm (s, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.1, 160.1, 138.1, 133.0, 132.1, 130.0, 129.8, 128.2, 115.2 ppm; mp 116.0–116.7 °C.
Benzophenone (3qa): Following general procedure A, 3qa was isolated as a white solid with low melting point (42 mg, 93%), known compound. The NMR spectroscopic data agree with those described in ref.[81]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80–7.78 (m, 4 H), 7.57 (tt, $J = 8.4$, 1.2 Hz, 2H), 7.49–7.44 ppm (m, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.8, 137.6, 132.4, 130.1, 128.3 ppm.

Naphthalen-1-yl(phenyl)methanone (3ra): Following general procedure A, 3ra was isolated as a light yellow oil (52 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[81]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09–8.07 (m, 1 H), 7.99 (d, $J = 8.0$ Hz, 1 H), 7.92–7.90 (m, 1 H), 7.87–7.84 (m, 2 H), 7.60–7.56 (m, 2 H), 7.54–7.48 (m, 3 H), 7.47–7.42 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.0, 138.3, 136.3, 133.7, 133.2, 131.2, 130.9, 130.4, 128.4, 128.37, 127.7, 127.2, 126.4, 125.7, 124.3 ppm.

Phenyl(thiophen-3-yl)methanone (3sa): Following general procedure A, 3sa was isolated as a light yellow oil (40 mg, 85%), known compound. The NMR spectroscopic data agree with those described in ref.[85]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91 (dd, $J = 2.8$, 1.2 Hz, 1 H), 7.84–7.82 (m, 2 H), 7.59–7.55 (m, 2 H), 7.49–7.45 (m, 2 H), 7.36 ppm (dd, $J = 5.2$, 2.8 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.0, 141.3, 138.6, 133.9, 132.3, 129.3, 128.6, 128.4, 126.2 ppm.

(3,5-Dimethylisoxazol-4-yl)(phenyl)methanone (3ta): Following general procedure A, 3ta was isolated as a colorless liquid (45 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[82]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.70–7.68 (m, 2 H), 7.59 (tt, $J = 7.2$, 1.2 Hz, 1H), 7.50–7.46 (m, 2 H), 2.31 (s, 3 H), 2.28 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.4, 172.3, 159.6, 138.4, 133.2, 128.9, 128.8, 116.5, 13.3, 11.3 ppm.
Phenyl(pyridin-4-yl)methanone (3ua): Following general procedure A except that the amount of PivOH is 0.25 mmol, 3ua was isolated as a light yellow solid (32 mg, 72%), known compound. The NMR spectroscopic data agree with those described in ref.[S7]. \( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.79 (d, \( J = 4.8 \) Hz, 2 H), 7.80 (d, \( J = 7.2 \) Hz, 2 H), 7.63 (t, \( J = 7.2 \) Hz, 1 H), 7.57 (d, \( J = 5.6 \) Hz, 2 H), 7.49 ppm (t, \( J = 8.0 \) Hz, 2 H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 195.1, 150.2, 144.5, 135.8, 133.6, 130.1, 128.6, 122.9 ppm; mp 63.7–64.4 °C.

(4-Chlorophenyl)(2,4-dimethylphenyl)methanone (3ab): Following general procedure A, 3ab was isolated as a light yellow oil (52 mg, 85%), known compound (CAS 57800-67-6). \( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.71 (d, \( J = 8.8 \) Hz, 2 H), 7.40 (d, \( J = 8.8 \) Hz, 2 H), 7.19 (d, \( J = 8.8 \) Hz, 1 H), 7.09 (s, 1 H), 7.03 (d, \( J = 8.8 \) Hz, 1 H), 2.36 (s, 3 H), 2.30 ppm (s, 3 H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 197.2, 141.0,139.3, 137.3, 136.5, 135.1, 132.0, 131.4, 129.1, 128.7, 125.9, 21.4, 20.1 ppm.

(2,4-Dimethylphenyl)(phenyl)methanone (3qb): Following general procedure A, 3qb was isolated as a light yellow oil (42 mg, 81%), known compound. The NMR spectroscopic data agree with those described in ref.[S8]. \( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.78–7.76 (m, 2 H), 7.55 (tt, \( J = 7.2, 2.0 \) Hz, 1H), 7.43 (t, \( J = 8.0 \) Hz, 2 H), 7.22 (d, \( J = 8.0 \) Hz, 1 H), 7.09 (s, 1 H),7.03 (d, \( J = 8.0 \) Hz, 1 H), 2.37 (s, 3 H), 2.31 ppm (s, 3 H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 198.6, 140.6, 138.2, 137.3, 135.6, 132.8, 131.9, 130.1, 129.2, 128.3, 125.8, 21.4, 20.1 ppm.

(2,4-Dimethylphenyl)(o-tolyl)methanone (3lb): Following general procedure A, 3lb was isolated as a light yellow oil (48 mg, 86%), known compound (CAS 13152-98-2). \( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.35 (td, \( J = 7.2, 1.6 \) Hz, 1H), 7.28–7.23 (m, 2 H), 7.23–7.16 (m, 2 H), 7.08 (s, 1 H), 6.97 (d, \( J = 8.0 \) Hz, 1 H), 2.44 (s, 3 H), 2.38 (s, 3 H), 2.35 ppm (s, 3 H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 200.6, 141.8, 139.7, 138.8, 137.6, 135.8, 132.4, 132.2, 131.2, 130.6, 129.7, 126.0, 125.3, 21.4, 20.9, 20.4 ppm.
(2,4-Dimethylphenyl)(4-methoxyphenyl)methanone (3ob): Following general procedure A, 3ob was isolated as a light yellow oil (48 mg, 81%), known compound (CAS 57800-66-5). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.76 (d, $J = 8.8$ Hz, 2 H), 7.18 (d, $J = 7.6$ Hz, 1 H), 7.07 (s, 1 H), 7.02 (d, $J = 7.6$ Hz, 1 H), 6.90 (d, $J = 8.8$ Hz, 2 H), 3.85 (s, 3 H), 2.36 (s, 3 H), 2.27 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.4, 163.5, 140.1, 136.6, 136.2, 132.5, 131.7, 130.9, 128.6, 125.8, 113.6, 55.5, 21.4, 19.9 ppm.

(4-Chlorophenyl)(4-(hydroxymethyl)phenyl)methanone (3ac): Following general procedure A, 3ac was isolated as a light white solid (49 mg, 80%), known compound (CAS 183171-01-9). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J = 8.4$ Hz, 2 H), 7.71 (d, $J = 8.4$ Hz, 2 H), 7.47–7.42 (m, 4 H), 4.78 (s, 2 H), 2.26 ppm (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.2, 145.8, 138.9, 136.4, 135.9, 131.4, 130.2, 128.6, 126.5, 64.6 ppm; mp 127.6–128.2 °C.

(4-(Hydroxymethyl)phenyl)(phenyl)methanone (3qc): Following general procedure A, 3qc was isolated as a yellow solid with low melting point (41 mg, 79%), known compound. The NMR spectroscopic data agree with those described in ref.[S9]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80–7.76 (m, 4 H), 7.57 (tt, $J = 8.8$, 1.2 Hz, 1 H), 7.49–7.44 (m, 4 H), 4.79 (s, 2 H), 1.77 ppm (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.5, 145.5, 137.6, 136.8, 132.4, 130.4, 130.0, 128.3, 126.4, 64.7 ppm.

(4-(Hydroxymethyl)phenyl)(m-tolyl)methanone (3mc): Following general procedure A, 3mc was isolated as a light brown oil (40 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 8.4$ Hz, 2 H), 7.59 (s, 1 H), 7.54 (d, $J = 7.6$ Hz, 1 H), 7.46 (d, $J = 8.4$ Hz, 2 H), 7.39–7.32 (m, 2 H), 4.79 (s, 2 H), 2.40 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.8, 145.5, 138.2, 137.6, 136.9, 133.2, 130.4, 130.35, 128.1, 127.3, 126.4, 64.7, 21.3 ppm; HRMS (ESI) calcd for C$_{15}$H$_{14}$NO$_2$ [M+H] m/z 249.088601,
(4-(Hydroxymethyl)phenyl)(4-methoxyphenyl)methanone (3oc): Following general procedure A, 3oc was isolated as a light white solid (43 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 8.8$ Hz, 2 H), 7.73 (d, $J = 8.4$ Hz, 2 H), 7.44 (d, $J = 8.4$ Hz, 2 H), 6.94 (d, $J = 8.8$ Hz, 2 H), 4.77 (s, 2 H), 3.87 (s, 3 H), 1.86 ppm (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.3, 163.2, 144.9, 137.4, 132.5, 130.2, 130.1, 126.4, 113.6, 64.7, 55.5 ppm; HRMS (ESI) calcd for C$_{15}$H$_{14}$NO$_3$ [M+H] m/z 265.083515, found m/z 265.082937; IR: $\nu_{\text{max}}$ = 3462, 3186, 3020, 2970, 2914, 2850, 1648, 1598, 1510, 1464, 1412, 1372, 1316, 1260, 1164, 1142, 1050, 1018, 934, 848, 760, 686 cm$^{-1}$; mp 113.5–114.3 °C.

(4-(Tert-butyl)phenyl)(4-chlorophenyl)methanone (3ad): Following general procedure A, 3ad was isolated as a light yellow solid (61 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.$^{[S14]}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75–7.70 (m, 4 H), 7.48 (d, $J = 8.8$ Hz, 2 H), 7.43 (d, $J = 8.8$ Hz, 2 H), 1.35 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.2, 156.4, 138.6, 136.2, 134.4, 131.4, 130.0, 128.5, 125.3, 35.1, 31.1 ppm; mp 74.6–75.6 °C.

(4-(Tert-butyl)phenyl)(phenyl)methanone (3qd): Following general procedure A, 3qd was isolated as a light yellow oil (50 mg, 85%), known compound. The NMR spectroscopic data agree with those described in ref.$^{[S2]}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80–7.74 (m, 4 H), 7.56 (tt, $J = 7.6$, 1.2 Hz, 1 H), 7.49–7.44 (m, 4 H), 1.35 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.4, 156.2, 137.9, 134.8, 132.1, 130.1, 129.9, 128.2, 125.2, 35.1, 31.1 ppm.
(4-(Tert-butyl)phenyl)(o-tolyl)methanone (3ld): Following general procedure A, 3ld was isolated as a light yellow oil (56 mg, 90%), known compound. (CAS 14252-16-5). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (d, $J$ = 8.8 Hz, 4 H), 7.36 (dd, $J$ = 7.2, 1.2 Hz, 1 H), 7.30–7.20 (m, 3 H), 2.31 (s, 3 H), 1.33 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.3, 157.0, 138.9, 136.5, 135.0, 130.9, 130.1, 130.0, 128.3, 125.4, 125.1, 35.1, 31.1, 19.9 ppm.

(4-(Tert-butyl)phenyl)(m-tolyl)methanone (3md): Following general procedure A, 3md was isolated as a yellow oil (56 mg, 90%), known compound (CAS 55709-37-0). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J$ = 8.8 Hz, 2 H), 7.61 (s, 1 H), 7.56 (d, $J$ = 7.6 Hz, 1 H), 7.47 (d, $J$ = 8.8 Hz, 2 H), 7.38–7.32 (m, 2 H), 2.40 (s, 3 H), 1.35 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.7, 156.1, 138.0, 134.9, 132.9, 130.3, 130.1, 128.0, 127.3, 125.2, 35.1, 31.1, 21.3 ppm.

(4-(Tert-butyl)phenyl)(4-methoxyphenyl)methanone (3od): Following general procedure A, 3od was isolated as a colorless oil (50 mg, 75%), known compound. The NMR spectroscopic data agree with those described in ref.$^{[S16]}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J$ = 8.8 Hz, 2 H), 7.70 (d, $J$ = 8.8 Hz, 2 H), 7.47 (d, $J$ = 8.8 Hz, 2 H), 6.94 (d, $J$ = 8.8 Hz, 2 H), 3.86 (s, 3 H), 1.35 ppm (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.3, 163.0, 155.5, 135.4, 132.4, 130.4, 129.8, 125.1, 113.4, 55.4, 35.0, 31.1 ppm.

Bis(4-chlorophenyl)methanone (3ae): Following general procedure A, 3ae was isolated as a light white solid (51 mg, 82%), known compound. The NMR spectroscopic data agree with those described in ref.$^{[S10]}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.70 (d, $J$ = 8.8 Hz, 4 H), 7.45 ppm (d, $J$ = 8.8 Hz, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 194.2, 139.1, 135.5, 131.3, 128.7 ppm.; mp 144.6–145.4 °C.
(4-Chlorophenyl)(o-tolyl)methanone (3lc): Following general procedure A, 3lc was isolated as a colorless liquid (46 mg, 80%), known compound. The NMR spectroscopic data agree with those described in ref.[S11]. 

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, $J = 8.8$ Hz 2 H), 7.41 (d, $J = 8.8$ Hz, 2 H), 7.38–7.36 (m, 1 H), 7.29–7.21 (m, 3 H), 2.30 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.3, 139.7, 138.1, 136.8, 136.1, 131.5, 131.1, 130.5, 128.8, 128.4, 125.3, 19.9 ppm.

(4-Chlorophenyl)(m-tolyl)methanone (3me): Following general procedure A, 3me was isolated as a light white solid (50 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S11]. 

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.73 (d, $J = 8.4$ Hz 2 H), 7.57 (s, 1 H); 7.52 (d, $J = 7.6$ Hz, 1 H), 7.44 (d, $J = 8.4$ Hz, 2 H), 7.40–7.33 (m, 2 H), 2.40 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 195.7, 138.8, 138.3, 137.3, 136.0, 133.4, 131.4, 130.3, 128.6, 128.2, 127.2, 21.3 ppm; mp 102.6–102.8 °C.

(4-Chlorophenyl)(4-methoxyphenyl)methanone (3oe): Following general procedure A, 3oe was isolated as a light white solid (45 mg, 74%), known compound. The NMR spectroscopic data agree with those described in ref.[S12]. 

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.77 (d, $J = 8.8$ Hz 2 H), 7.68 (d, $J = 8.8$ Hz, 2 H), 7.43 (d, $J = 8.8$ Hz, 2 H), 6.95 (d, $J = 8.8$ Hz, 2 H), 3.87 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 194.2, 163.4, 138.2, 136.5, 132.4, 131.1, 129.8, 128.5, 113.7, 55.5 ppm; mp 123.8–124.1 °C.

(4-Chlorophenyl)(3-fluorophenyl)methanone (3af): Following general procedure A, 3af was isolated as a light white solid (48 mg, 83%), known compound (CAS 46698-36-6). 

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.73 (d, $J = 8.8$ Hz, 2 H), 7.52 (dt, $J = 7.6$, 1.2 Hz, 1 H), 7.47–7.42 (m, 4 H), 7.28 ppm (td, $J = 8.4$, 2.4, 1.2 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 194.0 (d, $J = 2.2$ Hz, 1 H).
Hz), 162.5 (d, \( J = 247 \) Hz), 139.3, 139.2, 135.3, 131.4, 130.1 (d, \( J = 7.7 \) Hz), 128.8, 125.7 (d, \( J = 3 \) Hz), 119.6 (d, \( J = 21.2 \) Hz), 116.6 ppm (d, \( J = 22.4 \) Hz); mp 76.6–77.3 °C.

(3-Fluorophenyl)(o-tolyl)methanone (3lf): Following general procedure A, 3lf was isolated as a light yellow oil (42 mg, 80%), known compound (CAS 68295-41-0). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.53 (dt, \( J = 8.0, 1.2 \) Hz, 1 H), 7.51–7.48 (m, 1 H), 7.44–7.37 (m, 2 H), 7.30–7.22 (m, 4 H), 2.32 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 197.2 (d, \( J = 2.1 \) Hz), 162.7 (d, \( J = 246.6 \) Hz), 139.9 (d, \( J = 6.2 \) Hz), 137.9, 136.9, 131.2, 130.6, 130.1 (d, \( J = 7.6 \) Hz), 128.6, 126.0 (d, \( J = 3 \) Hz), 125.3, 120.1 (d, \( J = 21.4 \) Hz), 116.6 (d, \( J = 22.1 \) Hz), 20.0 ppm.

(3-Fluorophenyl)(m-tolyl)methanone (3mf): Following general procedure A, 3mf was isolated as a light yellow oil (49 mg, 93%), known compound (CAS 864087-22-9). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.60 (s, 1 H), 7.56 (dt, \( J = 8.4, 2.8, 1.2 \) Hz, 1 H), 7.49–7.42 (m, 2 H), 7.41–7.33 (m, 2 H), 7.26 (tdd, \( J = 8.4, 2.8, 1.2 \) Hz, 1 H), 2.41 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 195.5 (d, \( J = 2.0 \) Hz), 162.5 (d, \( J = 246.5 \) Hz), 139.8 (d, \( J = 6.4 \) Hz), 138.3, 137.1, 133.5, 130.4, 129.9 (d, \( J = 7.6 \) Hz), 128.2, 127.3, 125.8 (d, \( J = 3 \) Hz), 119.3 (d, \( J = 21.3 \) Hz), 116.7 (d, \( J = 22.3 \) Hz), 21.3 ppm.

(3-Fluorophenyl)(4-methoxyphenyl)methanone (3of): Following general procedure A, 3of was isolated as a light white solid (43 mg, 76%), known compound (CAS 96719-99-2). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.80 (d, \( J = 9.2 \) Hz, 2 H), 7.50 (dt, \( J = 7.6, 1.2 \) Hz, 2 H), 7.45–7.40 (m, 2 H), 7.24 (tdd, \( J = 8.4, 2.8, 1.2 \) Hz, 1 H), 6.95 (d, \( J = 9.2 \) Hz, 2 H), 3.87 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 194.0 (d, \( J = 2.0 \) Hz), 163.5, 162.4 (d, \( J = 246 \) Hz), 140.4 (d, \( J = 6.2 \) Hz), 132.5, 129.9, 129.7 (d, \( J = 23.6 \) Hz), 125.4 (d, \( J = 2.9 \) Hz), 118.8 (d, \( J = 21.2 \) Hz), 116.5 (d, \( J = 22.2 \) Hz), 113.7, 55.5 ppm; mp 68.1–68.6 °C.
(4-Chlorophenyl)(4-fluorophenyl)methanone (3ag): Following general procedure A, 3ag was isolated as a light white solid (53 mg, 91%), known compound. The NMR spectroscopic data agree with those described in ref. [S14]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81–7.78 (m, 2 H), 7.70 (d, $J = 8.4$ Hz, 2 H), 7.45 (d, $J = 8.4$ Hz, 2 H), 7.15 ppm (t, $J = 8.4$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 194.0, 165.5 (d, $J = 253.1$ Hz), 139.0, 135.8, 133.4 (d, $J = 3$ Hz), 132.5 (d, $J = 9.1$ Hz), 131.3, 128.7, 115.6 ppm (d, $J = 21.8$ Hz); mp 112.1–112.7 °C.

(4-Fluorophenyl)(o-tolyl)methanone (3lg): Following general procedure A, 3lg was isolated as a light yellow oil (48 mg, 90%), known compound (CAS 68295-42-1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83–7.79 (m, 2 H), 7.40–7.36 (m, 1 H), 7.28–7.21 (m, 3 H), 7.13–7.09 (m, 2 H), 2.30 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.1, 165.8 (d, $J = 253.7$ Hz), 138.4, 136.6, 134.1 (d, $J = 3$ Hz), 132.7 (d, $J = 9$ Hz), 131.1, 130.3, 128.3, 125.3, 115.6 (d, $J = 22$ Hz), 19.9 ppm.

(4-Fluorophenyl)(m-tolyl)methanone (3mg): Following general procedure A, 3mg was isolated as a light yellow oil (48 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref. [S17]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84–7.80 (m, 2 H), 7.57 (s, 1 H), 7.52 (d, $J = 7.6$ Hz, 1 H), 7.40–7.36 (m, 2 H), 7.16–7.11 (m, 2 H), 2.41 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.5, 165.3 (d, $J = 252.5$ Hz), 138.3, 137.5, 133.9 (d, $J = 3.1$ Hz), 133.2, 132.6 (d, $J = 9.1$ Hz), 130.3, 128.1, 127.1, 115.4 (d, $J = 21.7$ Hz), 21.3 ppm.

(4-Fluorophenyl)(4-methoxyphenyl)methanone (3og): Following general procedure A, 3og was isolated as a light white solid (53 mg, 91%), known compound. The NMR spectroscopic data agree with those described in ref. [S18]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (dt, $J = 8.8$, 2.8 Hz, 4 H), 7.13 (t, $J = 8.8$ Hz, 2 H), 6.95 (d, $J = 8.8$ Hz, 2 H), 3.87 ppm (s, 3 H); $^{13}$C NMR
(100 MHz, CDCl$_3$): $\delta$ 194.1, 165.0 (d, $J = 251.5$ Hz), 163.2, 134.4 (d, $J = 3.1$ Hz), 132.4, 132.3 (d, $J = 8.9$ Hz), 130.0, 115.3 (d, $J = 21.6$ Hz), 113.6, 55.5 ppm; mp 92.0–92.5 °C.

(4-Chlorophenyl)(naphthalen-2-yl)methanone (3ah): Following general procedure A, 3ah was isolated as a light white solid (51 mg, 77%), known compound. The NMR spectroscopic data agree with those described in ref.$^{[S13]}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.21 (s, 1 H), 7.95–7.88 (m, 4 H), 7.79 (d, $J = 8.8$ Hz, 2 H), 7.63–7.53 (m, 2 H), 7.48 ppm (d, $J = 8.4$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.5, 138.8, 136.2, 135.3, 134.5, 132.2, 131.7, 131.5, 129.4, 128.7, 128.5, 128.4, 127.8, 126.9, 125.6 ppm; mp 122.3–123.1 °C.

4-(2-Naphthoyl)benzonitrile (3fh): Following general procedure A, 3fh was isolated as a light white solid (52 mg, 81%), known compound. (CAS 194939-76-9). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19 (d, $J = 1.2$ Hz, 1 H), 7.95 (d, $J = 8.4$ Hz, 1 H), 7.91–7.89 (m, 5 H), 7.79 (d, $J = 8.4$ Hz, 2 H), 7.65–7.60 (m, 1 H), 7.58–7.54 ppm (m, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.0, 141.5, 135.5, 133.5, 132.21, 132.16, 132.1, 130.2, 129.5, 128.9, 128.7, 127.8, 127.1, 125.2, 118.0, 115.5 ppm; mp 121.7–122.3 °C.

Naphthalen-2-yl(\textit{m}-tolyl)methanone (3mh): Following general procedure A, 3mh was isolated as a light white solid (43 mg, 70%), known compound (CAS 418770-90-8). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25 (d, $J = 0.8$ Hz, 1 H), 7.93–7.89 (m, 4 H), 7.67 (s, 1 H), 7.63–7.58 (m, 2 H), 7.56–7.52 (m, 1 H), 7.43–7.36 (m, 2 H), 2.43 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.0, 138.2, 137.9, 135.2, 135.0, 133.1, 132.3, 131.8, 130.5, 129.4, 128.3, 128.2, 128.1, 127.8, 127.4, 126.7, 125.8, 21.4 ppm; mp 72.3–73.3 °C.
(4-Methoxyphenyl)(naphthalen-2-yl)methanone (3oh): Following general procedure A, 3oh was isolated as a light white solid (47 mg, 73%), known compound. The NMR spectroscopic data agree with those described in ref^[S14]. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (s, 1 H), 7.93–7.85 (m, 6 H), 7.60–7.51 (m, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 3.88 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 195.5, 163.2, 135.5, 135.0, 132.6, 132.2, 131.1, 130.4, 129.2, 128.1, 128.0, 127.8, 126.7, 125.8, 113.6, 55.5 ppm; mp 85.9–86.5 °C.

Naphthalen-1-yl(naphthalen-2-yl)methanone (3rh): Following general procedure A, 3rh was isolated as a light yellow solid (57 mg, 82%), known compound. The NMR spectroscopic data agree with those described in ref^[S3]. ¹H NMR (400 MHz, CDCl₃): δ 8.24 (s, 1 H), 8.11 (d, J = 8.4 Hz, 1 H), 8.07 (dd, J = 8.4, 2.0 Hz, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 7.95–7.92 (m, 2 H), 7.89 (d, J = 8.4 Hz, 1 H), 7.82 (d, J = 8.4 Hz, 1 H), 7.64 (dd, J = 7.2, 1.2 Hz, 1 H), 7.61–7.57 (m, 1 H), 7.56–7.47 ppm (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 198.0, 136.6, 135.7, 135.6, 133.7, 132.9, 132.3, 131.2, 131.0, 129.6, 128.6, 128.41, 128.4, 127.8, 127.7, 127.3, 126.8, 126.5, 125.7, 125.3, 124.4 ppm; mp 131.0–131.8 °C.

Isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (3ve): Following general procedure A except that the reaction temperature is 120°C, 3ve was isolated as a light yellow solid (72 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 8.8 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 5.10–5.04 (m, 1 H), 1.64 (s, 6 H), 1.18 ppm (d, J = 6.0 Hz, 6 H); ¹³C NMR (100 MHz, CDCl₃): δ 194.3, 173.1, 159.7, 138.3, 136.4, 131.9, 131.1, 130.2, 128.5, 117.2, 79.4, 69.3, 25.3, 21.5 ppm; mp 74.2–75.2 °C.
3-((4-Benzoylbenzyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopentaphenanthren-17-one (3wa): Following general procedure A except that the reaction temperature is 120°C, 3wa was isolated as a light yellow solid (92 mg, 80%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83−7.78 (m, 4 H), 7.58 (tt, $J$ = 7.2, 1.2 Hz, 1 H), 7.53 (d, $J$ = 8.4 Hz, 2 H), 7.47 (t, $J$ = 7.6 Hz, 2 H), 7.20 (d, $J$ = 8.4 Hz, 1 H), 6.78 (dd, $J$ = 8.4, 2.4 Hz, 1 H), 6.72 (d, $J$ = 2.8 Hz, 1 H), 5.12 (s, 2 H), 2.88 (dd, $J$ = 11.2, 4.8 Hz, 2 H), 2.49 (dd, $J$ = 18.8, 8.8 Hz, 1 H), 2.41−2.36 (m, 1 H), 2.78−2.21 (m, 1 H), 2.17−1.92 (m, 4 H), 1.66−1.37 (m, 6 H), 0.89 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 220.9, 196.3, 156.5, 142.0, 137.9, 137.5, 137.0, 132.6, 132.4, 130.4, 130.0, 128.3, 126.9, 126.4, 114.9, 112.3, 69.3, 50.4, 48.0, 44.0, 38.3, 35.8, 31.5, 29.6, 26.5, 25.9, 21.6, 13.8 ppm; IR: $\nu_{\text{max}}$ = 3088, 3050, 3028, 2960, 2930, 2864, 1739, 1652, 1612, 1570, 1500, 1454, 1414, 1376, 1274, 1254, 1164, 1056, 922, 856, 796, 738, 704 cm$^{-1}$; mp 170.0−170.8 °C.

1,4-Phenylenediphenylmethanone (3xa): A 25 mL Schlenk flask was charged with 3x (84.2 mg, 0.25 mmol), 2a (142.3 mg, 0.75 mmol), Na$_2$CO$_3$ (106.6 mg, 1.0 mmol), and PivOH (25.8 mg, 0.25 mmol), and PEG-400 (2 mL) before standard cycles (three times) of evacuation and back-filling with dry and pure carbon monoxide (balloon). The reaction mixture was stirred and heated at 100 °C in an oil bath for the indicated time. After completion of the reaction (observed by TLC), the mixture was cooled to room temperature, poured into a saturated aqueous NaCl solution (15 mL), and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel to give a light yellow solid 3xa (50 mg, 70%). The NMR spectroscopic data agree with those described in ref.$^{[S1]}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (s, 4 H), 7.83−7.81 (m, 4 H), 7.61 (tt, $J$ = 7.2, 1.2 Hz, 2 H), 7.52–7.48 ppm (m, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.0, 140.6, 136.9, 133.0, 130.1, 129.7, 128.5 ppm; mp 158.3−159.3 °C.
3. Effect of Transition Metals on The Carbonylative Cross Coupling

Table S1 The effect of transition metals on the carbonylative Suzuki coupling.\(^a\)

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield of 3aa (%)</th>
<th>Yield of 3a'a' (%)</th>
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<td>5</td>
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<td>56</td>
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</table>

\(^a\) Reaction conditions: catalyst (2 mol %), 1a (0.25 mmol), 2a (0.375 mmol), Na\(_2\)CO\(_3\) (0.5 mmol), PivOH (0.125 mmol), PEG-400 (2.0 mL), 100\(^\circ\)C, and 9 h.

As per general procedure A, four reactions of 1a (60.8 mg, 0.25 mmol), 2a (71.1 mg, 0.375 mmol), Na\(_2\)CO\(_3\) (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) were carried out, one as a control. A transition-metal catalyst [Pd(OAc)\(_2\) (1.1 mg, 0.005 mmol), Cu powder (0.3 mg, 0.005 mmol), NiCl\(_2\) (0.7 mg, 0.005 mmol), or FeCl\(_2\) (0.6 mg, 0.005 mmol)] was introduced to the reactions. All reaction mixtures were stirred at 100\(^\circ\)C and ambient pressure for 9 h.

Furthermore, ICP was carried out to analyze the model reaction system (including the solvent) and showed that the concentrations of Pd, Ni, and Fe were lower than the detection limits of the machine. Although 10 ppm Cu was observed, the addition of 2–6 times this amount of Cu (nanocopper) to the reaction system did not obviously affect the reaction rate. These results suggest that the potential catalysts such as Pd, Cu, Ni, and Fe are not involved in this transformation, discarding the slightest doubt of a transition-metal catalyzed process.

4. Mechanistic investigations

4.1 Effect of radical scavengers.

\[ \text{Scheme S1} \] Effect of radical scavengers.

S20
As per general procedure A, three reactions of 1a (60.8 mg, 0.25 mmol), 2a (71.1 mg, 0.375 mmol), Na$_2$CO$_3$ (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) were carried out, one as a control. A radical scavenger [TEMPO (39.9 mg, 0.25 mmol), TEMPO (79.7 mg, 0.5 mmol), or 1,1-Diphenylethylene (40 µL, 0.25 mmol)] was introduced to the reactions. All reaction mixtures were stirred at 100 °C and ambient pressure for 9 h.

**Control experiments**

\[
\begin{align*}
\text{BF}_3 \quad \text{K} & \quad \text{Na}_2\text{CO}_3 (2 \text{ equiv}) \\
2a & \text{PivOH (0.5 equiv)} \\
& \text{PEG-400, CO (balloon)} \\
& 100 {\circ}\text{C}, 9 \text{ h}
\end{align*}
\]

Following general procedure B, a reaction of 2a (71.1 mg, 0.375 mmol), Na$_2$CO$_3$ (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 °C and ambient pressure for 9 h.

\[
\begin{align*}
\text{Na}_2\text{CO}_3 (2 \text{ equiv}) & \\
2a & \text{PivOH (0.5 equiv)} \\
& \text{PEG-400, CO (balloon)} \\
& 100 {\circ}\text{C}, 9 \text{ h}
\end{align*}
\]

Following general procedure B, a reaction of 1a (60.8 mg, 0.25 mmol), Na$_2$CO$_3$ (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 °C and ambient pressure for 9 h.

**Competition Experiments.**

\[
\begin{align*}
\text{Na}_2\text{CO}_3 (4 \text{ equiv}) & \\
\text{PivOH (1 equiv)} \\
O_2 & \text{PEG-400, CO (balloon)} \\
100 {\circ}\text{C}, 12 \text{ h}
\end{align*}
\]

Following general procedure A, a reaction of 1b (63.5 mg, 0.25 mmol), 1n (55.6 mg, 0.25 mmol), 2a (142.3 mg, 0.75 mmol), Na$_2$CO$_3$ (106.6 mg, 1.0 mmol), and PivOH (25.8 mg, 0.25 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 °C and ambient pressure for 12 h.
Following *general procedure A*, a reaction of 1b (60.8 mg, 0.25 mmol), 2d (93.8 mg, 0.375 mmol), 2e (85.3 mg, 0.375 mmol), Na$_2$CO$_3$ (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in PEG-400 (2.0 mL) was carried out. The reaction mixture was stirred at 100 $^\circ$C and ambient pressure for 12 h.

**Reaction time profile studies.**

According to the below Figure S1, in first one hour, the reaction ran much fast and gave the desired product in 80% yield. And no induction period was observed.

![Figure S1 Yield versus time curve of the model reaction under normal conditions.](image)

**Effect of solvents**

![Diagram of reaction solvents](image)
As per general procedure A, two reactions of 1a (60.8 mg, 0.25 mmol), 2a (71.1 mg, 0.375 mmol), Na₂CO₃ (53.3 mg, 0.5 mmol), and PivOH (12.9 mg, 0.125 mmol) in solvents [PEG-400 (2.0 mL) and PEM-250 (2.0 mL)] were carried out, one as a control. All reaction mixtures were stirred at 100 °C and ambient pressure for 9 h.

A proposed mechanism:

In view of our findings and previous studies (See: R. Luque, D. J. Macquarrie, *Org. Biomol. Chem.* 2009, 7, 1627–1632), a tentative mechanism might be proposed for the carbonylative transformation (Scheme S2). Initially, a potassium aryl trifluoroborate in the presence of a base reacts with CO to form aryl acyl anion. Thereafter, the aryl acyl anion undergoes nucleophilic attack of an aryl halide to yield the desired product upon elimination of a halide anion. The above mentioned competition experiments reveal that the nucleophilic attack of an aryl halide is likely to be the rate limiting step. Meanwhile, such a mechanism would explain the decreased efficiency of electron-rich aryl halides, as they could stabilize the positive charge engendered in the C–X bond via an inductive effect. When CO doesn’t insert into the potassium aryl trifluoroborate in time, biaryl side product will be formed. Indeed, Suzuki coupling was reported to proceed successfully in the absence of a metal catalyst (See: N. E. Leadbeater, M. Marco, *Angew. Chem. Int. Ed.*, 2003, 42, 1407-1409).

![Scheme S2 Proposed mechanism of the transition-metal-free carbonylative Suzuki coupling.](image)

5. References


6. Copies of NMR Spectra

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

\[ \text{\( ^{13}C \) NMR (100MHz, CDCl}_3 \)} \]
$$\text{O}_2N$$

3ba

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

$$\text{O}_2N$$

3ba

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

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

\( ^{13}\text{C NMR} \ (100\text{MHz, DMSO-}d_6) \)
$^1$H NMR (400MHz, CDCl$_3$)

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

$\text{C NMR (100MHz, CDCl}_3\text{)}$
$\text{OF}_{3}\text{Cga}$

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

$\text{OF}_{3}\text{C}$

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

$\text{OF}_{3}\text{C}$

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

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

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

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

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

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

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

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

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

$^{13}$C NMR (100MHz, CDCl$_3$)
S43

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

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

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

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

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

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

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

$^{13}$C NMR (100MHz, CDCl$_3$)
$\text{H}_2\text{CO}$

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

$\text{O}$

$\text{CH}_3$

$\text{CH}_3$

$3\text{ob}$

$\text{H}_3\text{CO}$

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

$\text{O}$

$\text{CH}_3$

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

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

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

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

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

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

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

\[
\text{O} \quad \text{C(CH}_3\text{)}_3
\]

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

\[
\text{O} \quad \text{C(CH}_3\text{)}_3
\]
$^1$H NMR (400MHz, CDCl$_3$)

$^1$H NMR (400MHz, CDCl$_3$)

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

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

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

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

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

3le
$\text{H}_2\text{C-}
\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array}
\text{H}
\begin{array}{c}
\text{3me}
\end{array}

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

\begin{array}{c}
\text{H}_2\text{C-}
\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array}
\text{H}
\begin{array}{c}
\text{3me}
\end{array}
\end{array}

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

\begin{array}{c}
\text{H}_2\text{C-}
\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array}
\text{H}
\begin{array}{c}
\text{3me}
\end{array}
\end{array}
$^{1}$H NMR (400MHz, CDCl$_3$)

$^{13}$C NMR (100MHz, CDCl$_3$)
\[ \text{S64} \]

**1H NMR (400MHz, CDCl}_3\)**

![H NMR spectrum](image1)

**13C NMR (100MHz, CDCl}_3\)**

![C NMR spectrum](image2)

\[ \text{3af} \]

\[ \text{Cl} - \text{O} \]

\[ \text{F} \]

\[ \text{Cl} - \text{O} \]

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

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

$\text{H}_3\text{C} \quad \text{O} \quad \text{F}$

$\text{H}_3\text{C}$

$\text{O}$

$\text{F}$

$\text{C}$

$\text{H}_3\text{C}$

$\text{O}$

$\text{F}$

$\text{C}$

$\text{H}_3\text{C}$

$\text{O}$

$\text{F}$

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

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

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

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

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

$3$mg
$^{1}H$ NMR (400MHz, CDCl$_3$)

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

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

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

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

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

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

$\text{O}$

$\text{CH}_3$

$\text{O}$

$\text{CH}_3$

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$\text{CH}_3$

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$\text{CH}_3$

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$\text{CH}_3$

$\text{O}$

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

$^1$H NMR (400MHz, CDCl$_3$)