Supplementary Information

Cobalt-catalyzed arylation of aldimines via chelation-assisted C–H bond functionalization

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Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40–63 µm silica gel (Si 60, Merck). $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) NMR spectrometer. $^1$H and $^{13}$C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CHCl$_3$ (77.0 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 µm film thickness). Gas chromatography–mass spectrometry (GC–MS) analysis was performed on a Shimadzu GCMS-QP2010 system equipped with a capillary column, Rxi®-5Sil MS (Restek, 0.25 mm i.d. x 30 m, 0.25 µm film thickness). High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were measured on a Büchi M-565 apparatus and uncorrected.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Anhydrous cobalt(II) bromide (>99%) was purchased from Alfa Aesar, and was used as received. THF was distilled over Na/benzophenone. Grignard reagents except MeMgCl (purchased from Aldrich) were prepared from the corresponding halides and magnesium turnings in anhydrous THF and titrated before use. The 2-arylpyridine derivatives were prepared by nickel-catalyzed cross-coupling according to the procedure reported by Mongin et al. High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were measured on a Büchi M-565 apparatus and uncorrected.

The aldimines were prepared by condensation of the corresponding aldehydes and aniline or p-anisidine in EtOH.
Optimization of Reaction Conditions

Table S1. Screening conditions for the reaction of 1a with 2a or 2b

<table>
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<tr>
<th>Entry</th>
<th>Imine</th>
<th>Ligand</th>
<th>RMgX</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>IPr•HCl</td>
<td>tBuCH₂MgBr</td>
<td>84(^c)</td>
</tr>
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<td>2(^d)</td>
<td>2b</td>
<td>IPr•HCl</td>
<td>tBuCH₂MgBr</td>
<td>81(^c)</td>
</tr>
<tr>
<td>3</td>
<td>2a</td>
<td>IMes•HCl</td>
<td>tBuCH₂MgBr</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>2a</td>
<td>L1</td>
<td>tBuCH₂MgBr</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5</td>
<td>2a</td>
<td>L2</td>
<td>tBuCH₂MgBr</td>
<td>&lt;1</td>
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<td>6</td>
<td>2a</td>
<td>IPr•HCl</td>
<td>MeMgCl</td>
<td>14</td>
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<td>Me₃SiCH₂MgCl</td>
<td>4</td>
</tr>
<tr>
<td>10(^e)</td>
<td>2a</td>
<td>IPr•HCl</td>
<td>tBuCH₂MgBr</td>
<td>0</td>
</tr>
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</table>

\(^a\) The reaction was performed on a 0.3 mmol scale. \(^b\) Determined by GC using n-tridecane as an internal standard. \(^c\) Isolated yield. \(^d\) CoCl\(_2\) was used instead of CoBr\(_2\). The reaction time was 24 h. \(^e\) CoBr\(_2\) was omitted from the reaction.
Addition of 2-Arylpyridine to Aromatic Aldimine (Table 1)

A Typical Procedure: 4-Methoxy-N-(phenyl(2-(pyridin-2-yl)phenyl)methyl)aniline (3b). In a Schlenk tube were placed CoCl$_2$ (3.9 mg, 0.030 mmol), IPr•HCl (12.8 mg, 0.030 mmol), 2-phenylpyridine (1a, 43 µL, 0.30 mmol), and THF (0.64 mL). To the mixture was added a THF solution of tBuCH$_2$MgBr (0.63 M, 0.86 mL, 0.54 mmol) dropwise at 0 °C. After stirring for 30 min, (E)-N-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) was added. The resulting mixture was stirred at 60 °C for 24 h, and then allowed to room temperature. The reaction was quenched by sequential addition of Et$_2$O (1 mL) and saturated aqueous solution of NH$_4$Cl (1 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over MgSO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc/Et$_3$N = 10/1/0.1) to afford the title compound as a brown oil (89.0 mg, 81 %).

3b: $R_f$ 0.17 (hexane/EtOAc = 5/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.71 (s, 3H), 4.28 (brs, 1H), 5.88 (s, 1H), 6.51 (d, $J = 8.8$ Hz, 2H), 6.71 (d, $J = 8.8$ Hz, 2H), 7.13-7.22 (m, 7H), 7.36-7.40 (m, 3H), 7.53-7.59 (m, 2H), 8.65 (d, $J = 4.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 55.8, 59.7, 114.6, 114.8, 122.0, 124.4, 126.9, 127.4, 127.7, 128.2, 128.4, 128.9, 130.2, 136.4, 140.5, 141.2, 141.8, 143.1, 149.1, 152.0, 159.7; HRMS (ESI) Calcd for C$_{25}$H$_{23}$N$_2$O [M + H]$^+$ 367.1810, found 367.1812.

N-(Phenyl(2-(pyridin-2-yl)phenyl)methyl)aniline (3a): The typical procedure was applied to 2-phenylpyridine (1a, 43 µL, 0.30 mmol) and (E)-N-benzylideneaniline (2a, 65.2 mg, 0.36 mmol) using CoBr$_2$ (6.6 mg, 0.030 mmol) at 60 °C for 6 h. Silica gel chromatography (eluent: hexane/EtOAc/Et$_3$N = 10/1/0.1) of the crude product afforded the title compound as a yellow oil (84.3 mg, 84 %).

$R_f$ 0.15 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.56 (brs, 1H), 6.01 (s, 1H), 6.58(d, $J = 8.0$ Hz, 2H), 6.70 (t, $J = 7.2$ Hz, 1H), 7.11-7.23 (m, 9H), 7.39-7.44 (m, 3H), 7.55-7.59 (m, 2H), 8.66-8.67 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 59.0, 113.5, 117.4, 122.0, 124.3, 127.0, 127.4, 127.7, 128.2, 128.4, 128.9, 129.2, 130.3, 136.4, 140.5, 141.0, 142.9, 147.4, 149.1, 159.6; HRMS (ESI) Calcd for C$_{24}$H$_{21}$N$_2$ [M + H]$^+$ 337.1705, found 337.1702.
4-Methoxy-N-((5-methoxy-2-(pyridin-2-yl)phenyl)(phenyl)methyl)aniline (3c): The typical procedure was applied to 2-(4-methoxyphenyl)pyridine (1b, 55.6 mg, 0.30 mmol) and (E)-N-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 14 h. Silica gel chromatography (eluent: hexane/EtOAc/ \( \text{Et}_3\text{N} \) = 10/1/0.1–5/1/0.1) of the crude product afforded the title compound as a dark brown oil (90.4 mg, 76%).

\( R_f \) 0.15 (hexane/EtOAc = 5/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 3.71 (s, 3H), 3.79 (s, 3H), 4.28 (brs, 1H), 5.92 (s, 1H), 6.52 (app.d, \( J = 6.8 \) Hz, 2H), 6.71 (app.d, \( J = 6.8 \) Hz, 2H), 6.89 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 7.12-7.26 (m, 8H), 7.34 (d, \( J = 8.4 \) Hz, 1H), 7.53-7.57 (m, 1H), 8.61-8.63 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 55.4, 55.8, 59.7, 112.2, 114.1, 114.7, 114.8, 121.7, 124.4, 127.0, 127.7, 128.4, 131.6, 133.2, 136.3, 141.8, 142.9, 143.0, 149.1, 152.1, 159.5, 160.0; HRMS (ESI) Calcd for C\(_{26}\)H\(_{25}\)N\(_2\)O\(_2\) [M + H]\(^+\) 397.1916, found 397.1921.

N-((5-Fluoro-2-(pyridin-2-yl)phenyl)(phenyl)methyl)-4-methoxyaniline (3d): The typical procedure was applied to 2-(4-fluorophenyl)pyridine (1c, 52.0 mg, 0.30 mmol) and (E)-N-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 14 h. Silica gel chromatography (eluent: hexane/EtOAc/ \( \text{Et}_3\text{N} \) = 10/1/0.1–5/1/0.1) of the crude product afforded the title compound as a dark brown oil (73.3 mg, 64%).

\( R_f \) 0.15 (hexane/EtOAc = 5/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 3.71 (s, 3H), 4.12 (brs, 1H), 5.88 (s, 1H), 6.52 (app.d, \( J = 6.8 \) Hz, 2H), 6.71 (app.d, \( J = 6.8 \) Hz, 2H), 7.03-7.09 (m, 4H), 7.16-7.21 (m, 4H), 7.32-7.36 (m, 2H), 7.55-7.59 (m, 1H), 8.62-8.64 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 55.9, 59.7, 114.3 (d, \( ^2J_{C-F} = 21 \) Hz), 114.8, 114.90 (d, \( ^2J_{C-F} = 20 \) Hz), 114.91, 122.2, 124.5, 127.3, 127.8, 128.6 (two signals overlapping), 131.2 (d, \( ^2J_{C-F} = 8 \) Hz), 136.5, 141.5, 142.5, 144.1 (d, \( ^3J_{C-F} = 7 \) Hz), 149.2, 152.3, 158.9, 163.3 (d, \( ^3J_{C-F} = 246 \) Hz); HRMS (ESI) Calcd for C\(_{25}\)H\(_{22}\)FN\(_2\)O \([M + H]^+\) 385.1716, found 385.1719.

3-(((4-Methoxyphenyl)amino)(phenyl)methyl)-N,N-dimethyl-4-(pyridin-2-yl)aniline (3e): The typical procedure was applied to N,N-dimethyl-4-(pyridin-2-yl)aniline (1d, 59.5 mg, 0.30 mmol) and (E)-N-benzyldiene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/ \( \text{Et}_3\text{N} \) = 6/1/0.1–5/1/0.1) of the crude product afforded the title compound as a
brown solid (34.2 mg, 28%).
m.p. 125.0-126.1 °C; \( R_f \) 0.12 (hexane/EtOAc = 5/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 2.92 (s, 6H), 3.70 (s, 3H), 4.37 (brs, 1H), 5.92 (s, 1H), 6.51 (app.d, \( J = 6.8 \) Hz, 2H), 6.68-6.71 (m, 3H), 6.82 (d, \( J = 2.4 \)Hz, 1H), 7.09-7.18 (m, 7H), 7.26-7.31 (m, 1H), 7.52-7.54 (m, 1H), 8.57-8.59 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 40.6, 55.9, 60.1, 111.2, 112.4, 114.7, 114.8, 121.2, 124.3, 126.7, 127.7, 128.3, 128.9, 131.4, 136.2, 142.1, 142.2, 143.5, 149.0, 150.9, 152.0, 160.1; HRMS (ESI) Calcd for C\(_{27}\)H\(_{28}\)N\(_3\)O \[M + H\]^+ 410.2232, found 410.2230.

4-Methoxy-N-((4-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methyl)aniline (3f): The typical procedure was applied to 2-(2-methyl)pyridine (1e, 49 \( \mu \)L, 0.30 mmol) and (E)-\( N \)-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 16 h. Silica gel chromatography (eluent: hexane/EtOAc/\( \text{Et}_3\)N = 10/1/0.1) of the crude product afforded the title compound as a brown oil (53.9 mg, 47%).

\( R_f \) 0.25 (hexane/EtOAc = 5/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 2.38 (s, 3H), 3.71 (s, 3H), 4.26 (brs, 1H), 5.77 (s, 1H), 6.49 (app.d, \( J = 6.8 \) Hz, 2H), 6.70 (app.d, \( J = 6.8 \) Hz, 2H), 7.13-7.22 (m, 9H), 7.38 (d, \( J = 8.0 \) Hz, 1H), 7.54-7.58 (m, 1H), 8.63-8.65 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 21.2, 55.9, 59.5, 114.6, 114.8, 122.0, 124.3, 126.9, 127.8, 128.2, 128.4, 129.6, 130.9, 136.3, 137.0, 138.3, 140.4, 141.8, 143.3, 149.2, 152.0, 159.7; HRMS (ESI) Calcd for C\(_{26}\)H\(_{25}\)N\(_2\)O \[M + H\]^+ 381.1967, found 381.1969.

4-Methoxy-N-((3-methoxy-2-(pyridin-2-yl)phenyl)(phenyl)methyl)aniline (3g): The typical procedure was applied to 2-(2-methoxyphenyl)pyridine (1f, 52 \( \mu \)L, 0.30 mmol) and (E)-\( N \)-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/\( \text{Et}_3\)N = 10/1/0.1–3/1/0.1) of the crude product afforded the title compound as a dark brown oil (83.4 mg, 70%).

\( R_f \) 0.06 (hexane/EtOAc = 5/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 3.70 (s, 3H), 3.72 (s, 3H), 4.10 (d, \( J = 4.0 \) Hz, 1H), 5.31 (d, \( J = 4.4 \) Hz, 1H), 6.44 (app.d, \( J = 6.8 \) Hz, 2H), 6.67 (app.d, \( J = 6.8 \) Hz, 2H), 6.91 (d, \( J = 8.0 \) Hz, 1H), 6.96 (d, \( J = 7.6 \) Hz, 1H), 7.04-7.06 (m, 2H), 7.13-7.18 (m, 5H), 7.34 (t, \( J = 6.0 \) Hz, 1H), 7.51-7.53 (m, 1H), 8.62 (d, \( J = 4.0 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 55.88, 55.91, 60.2, 110.1, 114.6, 114.8, 120.0, 122.0, 126.2, 127.1, 127.8, 128.4, 128.9, 131.4, 136.2, 139.0, 140.4, 141.8, 143.3, 149.2, 152.0, 159.7; HRMS (ESI) Calcd for C\(_{26}\)H\(_{25}\)N\(_2\)O \[M + H\]^+ 381.1967, found 381.1969.
129.6, 129.7, 135.8, 141.9, 143.0, 149.4, 152.0, 156.3, 157.3; HRMS (ESI) Calcd for C_{26}H_{25}N_{2}O_{2} [M + H]^+ 397.1916, found 397.1920.

4-Methoxy-N-(phenyl(2-(pyridin-2-yl thiophen-3-yl)methyl)aniline (3h): The typical procedure was applied to 2-(thiophen-2-yl)pyridine (1g, 48.4 mg, 0.30 mmol) and (E)-N-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/ Et_{3}N = 10/1/0.1–7/1/0.1) of the crude product afforded the title compound as a dark brown solid (56.3 mg, 48%). m.p. 104.1-105.9 °C; R_{f} 0.33 (hexane/EtOAc = 5/1); \textsuperscript{1}H NMR (400 MHz, CDCl_{3}): \delta 3.70 (s, 3H), 4.25 (brs, 1H), 6.17 (s, 1H), 6.52 (app.d, J = 6.8 Hz, 2H), 6.71 (app.d, J = 6.8 Hz, 2H), 7.01 (d, J = 5.2 Hz, 1H), 7.15-7.18 (m, 1H), 7.26 (t, J = 6.8 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.61-7.63 (m, 1H), 8.63-8.65 (m, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl_{3}): \delta 55.8, 57.0, 114.7, 114.9, 122.0, 122.5, 126.2, 127.3, 127.5, 128.7, 129.6, 136.9, 139.4, 141.5, 141.9, 142.9, 149.7, 152.2, 152.8; HRMS (ESI) Calcd for C_{23}H_{21}N_{2}O [M + H]^+ 373.1375, found 373.1376.

4-Methoxy-N-((2-(4-methyl pyridin-2-yl)phenyl)(phenyl)methyl)aniline (3i): The typical procedure was applied to 4-methyl-2-phenylpyridine (1h, 50.8 mg, 0.30 mmol) and (E)-N-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/ Et_{3}N = 6/1/0.1) of the crude product afforded the title compound as a brown solid (76.3 mg, 67%). m.p. 126.4-127.3 °C; R_{f} 0.20 (hexane/EtOAc = 5/1); \textsuperscript{1}H NMR (400 MHz, CDCl_{3}): \delta 2.35 (s, 3H), 4.26 (brs, 1H), 5.85 (s, 1H), 6.49 (app.d, J = 6.8 Hz, 2H), 6.70 (app.d, J = 6.8 Hz, 2H), 7.09 (d, J = 8.0 Hz, 1H), 7.16-7.21 (m, 5H), 7.35-7.41 (m, 4H), 7.49-7.51 (m, 1H), 8.48 (dd, J = 1.4, 0.6 Hz, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl_{3}): \delta 18.3, 55.8, 59.6, 114.6, 114.8, 123.8, 126.9, 127.3, 127.7, 128.2, 128.4, 128.7, 130.2, 131.5, 136.9, 140.4, 141.2, 141.8, 143.2, 149.5, 152.0, 156.7; HRMS (ESI) Calcd for C_{26}H_{25}N_{2}O [M + H]^+ 381.1967, found 381.1962.

4-Methoxy-N-((5-methoxy-2-(3-methyl pyridin-2-yl)phenyl)(phenyl)methyl)aniline (3j): The typical procedure was applied to 2-(4-methoxyphenyl)-3-methylpyridine (1i, 56 µL, 0.30 mmol) and (E)-N-benzylidene-4-methoxyaniline (2b, 76.1 mg, 0.36 mmol) for 24 h. Silica gel
chromatography (eluent: hexane/EtOAc/Et$_3$N = 6/1/0.1) of the crude product afforded the title compound as a yellow oil (62.6 mg, 51%).

$R_f$ 0.16 (hexane/EtOAc = 5/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.63 (s, 3H), 3.70 (s, 3H), 3.80 (s, 3H), 4.32 (brs, 1H), 5.40 (s, 1H), 6.52 (brs, 2H), 6.70 (d, $J$ = 8.8 Hz, 2H), 6.85 (dd, $J$ = 8.4, 2.4 Hz, 1H), 6.93 (brs, 2H), 7.08-7.13 (m, 5H), 7.19-7.23 (m, 1H), 7.34 (d, $J$ = 8.0 Hz, 1H), 8.45-8.47 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 19.0, 55.5, 55.9, 60.8, 111.9, 114.7, 114.8, 122.4, 124.9, 127.1, 127.7, 128.4, 129.2, 130.7, 132.3, 132.9, 138.0, 141.9, 142.3, 146.5, 152.1, 158.8, 159.7; HRMS (ESI) Calcd for C$_{27}$H$_{27}$N$_2$O$_2$ [M + H]$^+$ 411.2073, found 411.2076.

$N$-((2-(1H-pyrazol-1-yl)phenyl)(phenyl)methyl)aniline (3k): The typical procedure was applied to 1-phenyl-1H-pyrazole (1j, 40 µL, 0.30 mmol) and (E)-N-benzylideneaniline (2b, 65.2 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/Et$_3$N = 15/1/0.1–10/1/0.1) of the crude product afforded the title compound as a light yellow oil (59.3 mg, 61%).

$R_f$ 0.42 (hexane/EtOAc = 5/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.35 (d, $J$ = 2.8 Hz, 1H), 5.85 (d, $J$ = 3.2 Hz, 1H), 6.30 (t, $J$ = 2.0 Hz, 1H), 6.50 (d, $J$ = 7.6 Hz, 2H), 6.72 (t, $J$ = 7.2 Hz, 1H), 7.08-7.10 (m, 2H), 7.12-7.16 (m, 2H), 7.21-7.25 (m, 4H), 7.35 (td, $J$ = 7.2, 1.6 Hz, 1H), 7.41 (td, $J$ = 7.2, 1.6 Hz, 1H), 7.44 (td, $J$ = 7.2, 1.6 Hz, 1H), 7.69 (dd, $J$ = 7.6, 1.6 Hz, 1H), 7.74 (d, $J$ = 1.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 57.6, 106.5, 113.6, 117.8, 127.2, 127.5, 127.6, 128.2, 128.59, 128.62, 129.26, 129.31, 131.2, 138.9, 139.5, 140.7, 142.1, 147.0; HRMS (ESI) Calcd for C$_{22}$H$_{20}$N$_3$ [M + H]$^+$ 326.1657, found 326.1658.

4-Methoxy-$N$-((2-(pyridin-2-yl)phenyl)(p-tolyl)methyl)aniline (3l): The typical procedure was applied to 2-phenylpyridine (1a, 43 µL, 0.30 mmol) and (E)-4-methoxy-$N$-(4-methylbenzylidene)aniline (2c, 81.1 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/Et$_3$N = 7/1/0.1) of the crude product afforded the title compound as a dark red solid (97.3 mg, 85%).

m.p. 89.3-91.6 ºC; $R_f$ 0.25 (hexane/EtOAc = 5/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.28 (s, 3H), 3.69 (s, 3H), 4.21 (brs, 1H), 5.83 (s, 1H), 6.49 (app.d, $J$ = 9.2 Hz, 2H), 6.69 (app.d, $J$ = 8.8 Hz, 2H), 7.02 (s, 4H), 7.18-7.23 (m, 2H), 7.33-7.39 (m, 3H), 7.53-7.56 (m, 2H), 8.62-8.64 (m, 1H);
13C NMR (100 MHz, CDCl3): δ 21.2, 55.8, 59.3, 114.6, 114.7, 122.0, 124.3, 127.2, 127.6, 128.0, 128.8, 129.1, 130.1, 136.3, 136.5, 136.6, 140.1, 140.4, 141.1, 141.8, 149.1, 151.9, 159.6; HRMS (ESI) Calcd for C26H25N2O [M + H]⁺ 381.1967, found 381.1970.

4-Methoxy-N-((4-methoxyphenyl)(2-(pyridin-2-yl)phenyl)methyl)aniline (3m): The typical procedure was applied to 2-phenylpyridine (1a, 43 μL, 0.30 mmol) and (E)-4-methoxy-N-(4-methoxybenzylidene)aniline (2d, 86.9 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/Et3N = 10/1/0.1–5/1/0.1) of the crude product afforded the title compound as a dark brown oil (92.8 mg, 78%).

Rf 0.13 (hexane/EtOAc = 5/1); 1H NMR (400 MHz, CDCl3): δ 3.71 (s, 3H), 3.75 (s, 3H), 4.22 (brs, 1H), 5.83 (s, 1H), 6.51 (d, J = 9.2 Hz, 2H), 6.71–6.75 (m, 4H), 7.04 (d, J = 8.4 Hz, 2H), 7.15–7.20 (m, 2H), 7.35–7.40 (m, 3H), 7.56–7.60 (m, 2H), 8.65 (d, J = 4.4 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 55.3, 55.8, 113.7, 114.6, 114.7, 121.9, 124.3, 127.2, 127.8, 128.8 (two signals overlapping), 130.1, 135.3, 136.3, 140.4, 141.3, 141.8, 149.1, 151.9, 158.5, 159.7; HRMS (ESI) Calcd for C26H25N2O2 [M + H]⁺ 397.1916, found 397.1918.

N-((4-Fluorophenyl)(2-(pyridin-2-yl)phenyl)methyl)-4-methoxyaniline (3n): The typical procedure was applied to 2-phenylpyridine (1a, 43 μL, 0.30 mmol) and (E)-N-(4-fluorobenzylidene)-4-methoxyaniline (2e, 82.5 mg, 0.36 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc/Et3N = 10/1/0.1–7/1/0.1) of the crude product afforded the title compound as a brown oil (30.4 mg, 26%).

Rf 0.17 (hexane/EtOAc = 5/1); 1H NMR (400 MHz, CDCl3): δ 3.71 (s, 3H), 4.25 (brs, 1H), 5.83 (s, 1H), 6.48 (app.d, J = 9.2 Hz, 2H), 6.70 (app.d, J = 9.2 Hz, 2H), 6.86 (t, J = 8.8 Hz, 2H), 7.06–7.09 (m, 2H), 7.15 (d, J = 8.0 Hz, 1H), 7.17–7.20 (m, 1H), 7.36–7.38 (m, 3H), 7.46–7.49 (m, 1H), 7.54–7.58 (m, 1H), 8.61–8.62 (m, 1H); 13C NMR (100 MHz, CDCl3): δ 55.9, 59.0, 114.7, 114.9, 115.2 (d, 2JCF = 21 Hz), 121.1, 124.3, 127.5, 128.2, 129.0, 129.3 (d, 3JCF = 8 Hz), 130.3, 136.5, 138.9 (d, 4JCF = 3 Hz), 140.5, 141.1, 141.6, 149.1, 152.2, 159.7, 161.8 (d, 1JCF = 244 Hz); HRMS (ESI) Calcd for C25H22FN2O [M + H]⁺ 385.1716, found 385.1718.

4-Methoxy-N-((2-(pyridin-2-yl)phenyl)(m-tolyl)methyl)aniline (3o): The typical procedure was applied to 2-phenylpyridine (1a, 43 μL, 0.30 mmol) and
(E)-4-methoxy-N-(3-methylbenzylidene)aniline (2f, 81.1 mg, 0.36 mmol) for 13 h. Silica gel chromatography (elucon: hexane/EtOAc/Et3N = 7/1/0.1) of the crude product afforded the title compound as a dark red oil (87.8 mg, 77%).

\[ \text{Rf} \ 0.20 \ (hexane/EtOAc = 5/1); \] \[ ^1 \text{H NMR (400 MHz, CDCl}_3\text{)}: \delta \ 2.24 \ (s, 3H), 3.71 \ (s, 3H), 4.21 \ (brs, 1H), 5.82 \ (s, 1H), 6.51 \ (app.d, J = 9.2 Hz, 2H), 6.71 \ (app.d, J = 9.2 Hz, 2H), 6.93 \ (d, J = 6.8 Hz, 1H), 6.99 \ (d, J = 7.2 Hz, 1H), 7.09 \ (t, J = 7.6 Hz, 1H), 7.16-7.21 \ (m, 2H), 7.36-7.40 \ (m, 3H), 7.53-7.58 \ (m, 2H), 8.65-8.66 \ (m, 1H); \] \[ ^13 \text{C NMR (100 MHz, CDCl}_3\text{)}: \delta \ 21.5, 55.8, 59.7, 114.6, 114.8, 122.0, 124.4, 124.8, 127.3, 127.7, 128.1, 128.3, 128.4, 128.9, 130.1, 136.3, 137.9, 140.5, 141.3, 141.9, 143.0, 149.1, 152.0, 159.7; \] \[ \text{HRMS (ESI) Calcd for C}_{26}H_{25}N_2O [M + H]^+ 381.1967, found 381.1962. \]

4-Methoxy-N-((2-(pyridin-2-yl)phenyl)(o-toly)methyl)aniline (3p): The typical procedure was applied to 2-phenylpyridine (1a, 43 μL, 0.30 mmol) and (E)-4-methoxy-N-(2-methylbenzylidene)aniline (2g, 81.1 mg, 0.36 mmol) for 24 h. Silica gel chromatography (elucon: hexane/EtOAc/Et3N = 10/1/0.1–5/1/0.1) of the crude product afforded the title compound as a light yellow solid (88.3 mg, 77%).

\[ \text{m.p. 120.0-121.3 ℃; Rf} \ 0.19 \ (hexane/EtOAc = 5/1); \] \[ ^1 \text{H NMR (400 MHz, CDCl}_3\text{)}: \delta \ 1.96 \ (s, 3H), 3.71 \ (s, 3H), 4.07 \ (brs, 1H), 5.85 \ (s, 1H), 6.45 \ (app.d, J = 8.8 Hz, 2H), 6.71 \ (app.d, J = 9.2 Hz, 2H), 7.05-7.06 \ (m, 1H), 7.10-7.15 \ (m, 2H), 7.14-7.17 \ (m, 2H), 7.25-7.27 \ (m, 1H), 7.36-7.39 \ (m, 2H), 7.43-7.46 \ (m, 2H), 7.50-7.52 \ (m, 1H), 8.60 \ (d, J = 4.4 Hz, 1H); \] \[ ^13 \text{C NMR (100 MHz, CDCl}_3\text{)}: \delta \ 19.1, 55.8, 56.7, 114.1, 114.8, 121.9, 124.0, 126.0, 127.1, 127.4, 127.6, 128.2, 128.7, 130.0, 130.5, 136.2, 136.3, 139.9, 140.8, 140.9, 141.8, 149.2, 151.9, 159.5; \] \[ \text{HRMS (ESI) Calcd for C}_{26}H_{25}N_2O [M + H]^+ 381.1967, found 381.1972. \]

4-Methoxy-N-((2-methoxyphenyl)(2-(pyridin-2-yl)phenyl)methyl)aniline (3q): The typical procedure was applied to 2-phenylpyridine (1a, 43 μL, 0.30 mmol) and (E)-4-methoxy-N-(2-methoxybenzylidene)aniline (2h, 86.9 mg, 0.36 mmol) for 24 h. Silica gel chromatography (elucon: hexane/EtOAc/Et3N = 10/1/0.1–5/1/0.1) of the crude product afforded the title compound as a dark brown oil (62.9 mg, 53%).

\[ \text{Rf} \ 0.13 \ (hexane/EtOAc = 5/1); \] \[ ^1 \text{H NMR (400 MHz, CDCl}_3\text{)}: \delta \ 3.52 \ (s, 3H), 3.70 \ (s, 3H), 4.22 \ (brs, 1H), 5.99 \ (s, 1H), 6.44 \ (app.d, J = 8.8 Hz, 2H), 6.67 \ (app.d, J = 8.8 Hz, 2H), 6.72 \ (d, J =
8.0 Hz, 1H), 6.84 (t, \( J = 7.2 \) Hz, 1H), 7.14-7.18 (m, 2H), 7.25-7.27 (m, 2H), 7.32-7.34 (m, 2H), 7.39-7.41 (m, 2H), 7.54-7.58 (m, 1H), 8.61-8.62 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 54.1, 55.3, 55.9, 110.6, 114.5, 114.8, 120.6, 121.8, 124.1, 127.2, 128.0, 128.21, 128.24, 128.6, 130.0, 130.9, 136.0, 140.76, 140.79, 141.9, 149.2, 151.9, 156.9, 159.7; HRMS (ESI) Calcd for C\(_{26}\)H\(_{25}\)N\(_2\)O\(_2\) [M + H]\(^+\) 397.1916, found 397.1911.

\( N - ([1,1'\text{-Biphenyl}] - 2\text{-yl}(2\text{-pyridin-2-yl})\text{phenyl})\text{methyl})\text{-4-methoxyaniline (3r):} \) The typical procedure was applied to 2-phenylpyridine (1a, 43 \( \mu \)L, 0.30 mmol) and (\( E \))-\( N - ([1,1'\text{-biphenyl}] - 2\text{-ylmethylene})\text{-4-methoxyaniline (2i, 103.4 mg, 0.36 mmol) for 48 h. Silica gel chromatography (eluent: hexane/EtOAc/Et\(_3\)N = 10/1/0.1–7/1/0.1) of the crude product afforded the title compound as a light yellow solid (46.7 mg, 35%).

m.p. 142.1-143.1 °C; \( R_f \) 0.16 (hexane/EtOAc = 5/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 3.71 (s, 3H), 4.22 (brs, 1H), 5.69 (s, 1H), 6.41 (app.d, \( J = 8.8 \) Hz, 2H), 6.67 (app.d, \( J = 8.8 \) Hz, 2H), 6.73 (d, \( J = 7.6 \) Hz, 1H), 6.90 (d, \( J = 7.2 \) Hz, 2H), 6.99-7.01 (m, 1H), 7.12-7.16 (m, 3H), 7.20 (d, \( J = 7.6 \) Hz, 1H), 7.24-7.27 (m, 3H), 7.28-7.32 (m, 2H), 7.34-7.47 (m, 2H), 7.47-7.49 (m, 1H), 8.27-8.28 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 55.8, 57.0, 114.5, 114.7, 121.6, 123.5, 126.9, 127.0, 127.3, 127.6, 128.0, 128.3, 128.4, 128.7, 129.1, 130.1, 130.4, 135.9, 139.9, 140.7, 140.8, 141.0, 141.5, 141.9, 149.0, 151.9, 159.0; HRMS (ESI) Calcd for C\(_{31}\)H\(_{27}\)N\(_2\)O [M + H]\(^+\) 443.2123, found 443.2127.
Formation of Isoindolinones via Self-Coupling of Aldimine (Scheme 2)

In a Schlenk tube were placed CoBr$_2$ (6.6 mg, 0.030 mmol), IPr•HCl (12.8 mg, 0.030 mmol), ($E$)-4-methoxy-N-(1-(p-tolyl)ethylidene)aniline (2c, 67.6 mg, 0.30 mmol), and THF (0.64 mL). To the mixture was added a THF solution of tBuCH$_2$MgBr (0.63 M, 0.86 mL, 0.54 mmol) dropwise at 0 °C. After stirring for 30 min, another portion of 2c (67.6 mg, 0.30 mmol) was added. The resulting mixture was stirred at 60 °C for 6 h, and then allowed to room temperature. The reaction was quenched by the addition of ether (1 mL) and H$_2$O (1 mL), followed by dilution with ethyl acetate (3 mL). The resulting mixture was stirred under air for 96 h, and then extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over MgSO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc = 5/1 to 3/1 to 1/1) to afford 2-(4-methoxyphenyl)-5-methyl-3-(p-tolyl)isoindolin-1-one (5, 16.3 mg, 16%) and 3-hydroxy-2-(4-methoxyphenyl)-5-methyl-3-(p-tolyl)isoindolin-1-one (6, 52.8 mg, 49%) both as off-white solids. Note that GC-MS analysis of the crude mixture obtained just after quenching gave a major peak at $m/z$ = 327, indicating the formation of isoindole 4 (see Scheme 2). Attempted isolation of 4 by silica gel chromatography was not successful, resulting in the formation of 5, 6, and other intractable products.

**2-(4-Methoxyphenyl)-5-methyl-3-(p-tolyl)isoindolin-1-one (5):** m.p. 161.3-162.4 ºC; $R_f$ 0.29 (hexane/EtOAc = 3/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.28 (s, 3H), 2.38 (s, 3H), 3.75 (s, 3H), 5.91 (s, 1H), 6.82 (app.d, $J$ = 8.8 Hz, 2H), 7.01 (s, 1H), 7.04-7.09 (m, 4H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.42 (app.d, $J$ = 8.8 Hz, 2H), 7.83 (d, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 21.3, 22.1, 55.5, 66.0, 114.3, 123.5, 123.9, 124.8, 127.3, 129.0, 129.7, 129.9, 130.9, 135.0, 138.3, 143.2, 146.4, 157.1, 168.1; HRMS (ESI) Calcd for C$_{23}$H$_{22}$NO$_2$ [M + H]$^+$ 344.1651, found 344.1650.

**3-Hydroxy-2-(4-methoxyphenyl)-5-methyl-3-(p-tolyl)isoindolin-1-one (6):** m.p. 208.8-210.1 ºC; $R_f$ 0.16 (hexane/EtOAc = 3/1); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 2.21 (s, 3H), 2.34 (s, 3H), 3.68 (s, 3H), 6.82 (app.d, $J$ = 9.2 Hz, 2H), 7.05-7.07 (m, 3H), 7.21 (app.d, $J$ = 8.4 Hz, 2H), 7.32-7.36 (m, 3H), 7.44 (s, 1H), 7.69 (d, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 21.1, 21.8, 55.6, 92.4, 114.0, 123.3, 123.5, 126.5, 128.0, 129.4 (two signals overlapping), 129.7, 130.5, 137.4, 138.9.
137.7, 143.8, 150.6, 157.6, 166.8; HRMS (ESI) Calcd for C_{23}H_{22}NO_{3} [M + H]^+ 360.1600, found 360.1596.

Synthesis of Indenones via Self-Coupling of Aldimines (Scheme 2 and Table 2)

A Typical Procedure: 2-(4-Methoxyphenyl)-5-methyl-3-(p-tolyl)-1H-inden-1-one (7a). In a Schlenk tube were placed CoBr$_2$ (6.6 mg, 0.030 mmol), IPr•HCl (12.8 mg, 0.030 mmol), (E)-4-methoxy-N-(1-(p-tolyl)ethylidene)aniline (2c, 67.6 mg, 0.30 mmol), and THF (0.71 mL). To the mixture was added a THF solution of tBuCH$_2$MgBr (0.68 M, 0.79 mL, 0.54 mmol) dropwise at 0 °C. After stirring for 30 min, another portion of 2c (67.6 mg, 0.30 mmol) was added. The resulting mixture was stirred at room temperature for 12 h, followed by the addition of H$_2$O (0.3 mL) and 4-methoxybenzaldehyde (73 !L, 0.60 mmol). After stirring for 1 h, aq. HCl (3 M, 1 mL) was added, and the resulting mixture was stirred at 60 °C for 12 h. The reaction was cooled to room temperature, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over MgSO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc = 50/1) to afford the title compound as a red solid (72.0 mg, 71% based on 2c).

7a: m.p. 173.5-174.3 °C; R$_f$ 0.40 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 2.35 (s, 3H), 2.42 (s, 3H), 3.80 (s, 3H), 6.82 (app.d, $J$ = 8.8 Hz, 2H), 6.94 (s, 1H), 7.05 (d, $J$ = 7.2 Hz, 1H), 7.03-7.27 (m, 4H), 7.29 (app.d, $J$ = 8.0 Hz, 2H), 7.46 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 21.7, 22.3, 55.3, 113.8, 122.4, 123.0, 123.6, 128.6 (two signals overlapping), 128.7, 129.7, 130.3, 131.4, 132.1, 139.3, 144.4, 146.2, 153.8, 159.2, 196.9; HRMS (ESI) Calcd for C$_{24}$H$_{21}$O$_2$ [M + H]$^+$ 341.1542, found 341.1540.

2-(4-Methoxyphenyl)-3-phenyl-1H-inden-1-one (7b): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and 4-methoxybenzaldehyde (73 !L, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 50/1) of the crude product afforded the title compound as a light red solid (64.0 mg, 68%).

m.p. 116.8-117.5 °C (lit. 118-119 °C); R$_f$ 0.47 (hexane/EtOAc = 8/1); $^1$H NMR (400 MHz,
CDCl$_3$): $\delta$ 3.79 (s, 3H), 6.81 (app.d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.24-7.28 (m, 3H), 7.36 (t, $J = 7.2$ Hz, 1H), 7.39-7.44 (m, 5H), 7.57 (d, $J = 6.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 55.4, 113.8, 121.1, 123.0, 123.3, 128.7, 128.8, 129.0, 129.3, 130.9, 131.5, 132.1, 133.2, 133.6, 145.7, 154.0, 159.4, 197.2; HRMS (ESI) Calcd for C$_{22}$H$_{17}$O $[M + H]^+$ 313.1229, found 313.1226.

4-(1-Oxo-3-phenyl-1H-inden-2-yl)benzonitrile (7c): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and 4-cyanobenzaldehyde (78.7 mg, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 25/1) of the crude product afforded the title compound as a red solid (63.6 mg, 69%). m.p. 139.1-139.9 °C (lit. 142-144 °C); $^3$R$_f$ 0.27 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (d, $J = 7.2$ Hz, 1H), 7.34-7.37 (m, 4H), 7.38-7.41 (m, 2H), 7.43-7.47 (m, 3H), 7.53 (app.d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 7.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 111.2, 119.0, 122.1, 123.5, 128.5, 129.3, 129.9, 130.2, 130.5 (two signals overlapping), 130.7, 132.0, 132.1, 134.0, 135.9, 144.7, 158.0, 195.6; HRMS (ESI) Calcd for C$_{22}$H$_{14}$NO $[M + H]^+$ 308.1075, found 308.1078.

3-Phenyl-2-(4-(trifluoromethyl)phenyl)-1H-inden-1-one (7d): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and 4-trifluoromethylbenzaldehyde (82 µL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 100/1) of the crude product afforded the title compound as a light red oil (66.3 mg, 63%). $^3$R$_f$ 0.53 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (d, $J = 7.2$ Hz, 1H), 7.31-7.35 (m, 1H), 7.36-7.42 (m, 5H), 7.43-7.46 (m, 3H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 6.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 121.9, 123.5, 124.4 (q, $^1$J$_{C-H} =248$ Hz), 125.2 (q, $^3$J$_{C-H} =4.0$ Hz), 128.4 (q, $^2$J$_{C-H} =30$ Hz), 128.6, 129.3, 129.7, 130.0, 130.2, 130.4, 130.8, 132.4, 133.9, 134.7, 145.0, 157.3, 196.0; HRMS (ESI) Calcd for C$_{22}$H$_{14}$F$_{3}$O $[M + H]^+$ 351.0997, found 351.0999.

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2-(2,6-Difluorophenyl)-3-phenyl-1H-inden-1-one (7e): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and 2,6-difluorobenzaldehyde (65 µL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 50/1) of the crude product afforded the title compound as a yellow solid (76.6 mg, 80%). m.p. 133.3-134.5 °C; Rf 0.50 (hexane/EtOAc = 8/1); ¹H NMR (400 MHz, CDCl₃): δ 6.85-6.89 (m, 2H), 7.25-7.30 (m, 2H), 7.32-7.36 (m, 1H), 7.40-7.44 (m, 6H), 7.63 (d, J = 6.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 109.2 (t, ²J_C-F = 10 Hz), 111.7 (dd, ²J_C-F = 19 Hz, ⁴J_C-F = 6 Hz), 122.0, 123.5, 127.8, 128.9, 129.6, 130.1, 130.4 (t, ³J_C-F = 10 Hz), 131.5, 132.6, 133.5, 144.8, 144.8, 160.1, 161.0 (dd, ¹J_C-F = 249 Hz, ³J_C-F = 7 Hz), 194.4; HRMS (ESI) Calcd for C₂₁H₁₃F₂O [M + H]⁺ 319.0934, found 319.0933.

2-(4-Methoxyphenyl)-3-phenyl-1H-inden-1-one (7f): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and 3,5-diiodo-4-hydroxybenzaldehyde (224.3 mg, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 3/1) of the crude product afforded the title compound as a dark red solid (91.5 mg, 55%). m.p. 177.2-178.4 °C; Rf 0.55 (hexane/EtOAc = 3/1); ¹H NMR (400 MHz, CDCl₃): δ 5.82 (brs, 1H), 7.13 (d, J = 4.8 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.36-7.39 (m, 3H), 7.46-7.47 (m, 3H), 7.57 (d, J = 6.8 Hz, 1H), 7.59 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 81.9, 121.7, 123.3, 127.2, 128.5, 128.8, 129.2, 129.5, 130.0, 130.6, 132.2, 133.9, 140.7, 145.0, 153.2, 156.0, 196.1; HRMS (ESI) Calcd for C₂₁H₁₃I₂O₂ [M + H]⁺ 550.9005, found 550.9000.

3-Phenyl-2-(pyridin-4-yl)-1H-inden-1-one (7g): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and 4-pyridinecarboxaldehyde (56 µL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 5/1) of the crude product afforded the title compound as an orange solid (64.9 mg, 76%). m.p. 131.3-132.5 °C; Rf 0.20 (hexane/EtOAc = 3/1); ¹H NMR (400 MHz, CDCl₃): δ 7.17-7.18 (m, 3H), 7.34-7.47 (m, 7H), 7.61 (dd, J = 7.2, 0.8 Hz, 1H), 8.49 (d, J = 2.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 122.2, 123.5, 124.4, 128.4, 129.3, 129.7, 130.0, 130.2, 130.8, 132.0, 133.9, 138.9, 144.7, 149.8, 158.7, 195.4; HRMS (ESI) Calcd for C₂₀H₁₄NO [M + H]⁺ 284.1075,
found 284.1078.

2-(Furan-2-yl)-3-phenyl-1H-inden-1-one (7h): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and furfural (50 μL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 50/1) of the crude product afforded the title compound as a dark red solid (27.3 mg, 33%).

m.p. 92.3-93.7 ºC; Rf 0.55 (hexane/EtOAc = 8/1); ¹H NMR (400 MHz, CDCl₃): δ 6.43-6.44 (m, 1H), 7.02 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 3.2 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.26-7.27 (m, 1H), 7.32 (td, J = 7.6, 0.8 Hz, 1H), 7.47-7.50 (m, 6H);
¹³C NMR (100 MHz, CDCl₃): δ 111.7, 112.7, 121.7, 122.1, 123.2, 128.4, 128.8, 128.9, 129.4, 131.0, 133.2, 134.0, 143.1, 146.6, 147.3, 150.9, 146.6, 150.2; HRMS (ESI) Calcd for C₁₉H₁₃O₂ [M + H]+ 273.0916, found 273.0916.

Ethyl 1-oxo-3-phenyl-1H-indene-2-carboxylate (7i): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 126.8 mg, 0.60 mmol) and ethyl glyoxalate (50% solution in toluene, 120 μL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 30/1–10/1) of the crude product afforded the title compound as a yellow solid (34.0 mg, 41%).

m.p. 84.0-84.8 ºC (lit. 87-88 ºC); Rf 0.20 (hexane/EtOAc = 10/1); ¹H NMR (400 MHz, CDCl₃): δ 1.16 (t, J = 7.2 Hz, 3H), 4.20 (q, J = 6.8 Hz, 2H), 7.19-7.21 (m, 1H), 7.39-7.42 (m, 2H), 7.50-7.54 (m, 5H), 7.59-7.61 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 61.1, 123.6, 124.6, 128.3, 128.6, 130.6 (two signals overlapping) 130.7, 131.2, 131.7, 133.7, 143.3, 163.2, 165.1, 192.3; HRMS (ESI) Calcd for C₁₈H₁₅O₃ [M + H]+ 279.1021, found 279.0919.

5-Methoxy-2,3-bis(4-methoxyphenyl)-1H-inden-1-one (7j): The typical procedure was applied to (E)-4-methoxy-N-(4-methoxybenzylidene)aniline (2d, 144.8 mg, 0.60 mmol) and 4-methoxybenzaldehyde (73 μL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 15/1 – 5/1) of the crude product afforded the title compound as an orange solid (94.9 mg, 81%).

m.p. 169.4-170.1 ºC (lit. 173-175 ºC); Rf 0.21 (hexane/EtOAc = 8/1); ¹H NMR (400 MHz, CDCl₃): δ 3.78 (s, 3H), 3.81 (s, 3H), 3.83 (s, 3H), 3.83 (s, 3H),
6.63 (dd, J = 8.0, 2.0 Hz, 1H), 6.70 (d, J = 2.0 Hz, 1H), 6.81 (app.d, J = 8.0 Hz, 2H), 6.92 (app.d, J = 8.8 Hz, 2H), 7.24 (d, J = 9.2 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 55.3, 55.4, 55.8, 110.0, 110.3, 113.7, 114.3, 123.7, 123.8, 124.7, 125.2, 130.3, 131.4, 132.7, 148.2, 151.7, 159.2, 160.3, 164.4, 195.7; HRMS (ESI) Calcd for C24H21O4 [M + H]+ 373.1440, found 373.1439. The 1H and 13C NMR spectra showed good agreement with the literature data.

5-Fluoro-3-(4-fluorophenyl)-2-(4-methoxyphenyl)-1H-inden-1-one (7k): The typical procedure was applied to (E)-N-(4-fluorobenzylidene)-4-methoxyaniline (2e, 137.6 mg, 0.60 mmol) and 4-methoxybenzaldehyde (73 μL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 50/1) of the crude product afforded the title compound as a light red solid (59.6 mg, 57%). m.p. 180.4-181.3 °C; Rf 0.38 (hexane/EtOAc = 8/1); 1H NMR (400 MHz, CDCl3): δ 3.79 (s, 3H), 6.78-6.83 (m, 3H), 6.87-6.92 (m, 1H), 7.10-7.15 (m, 2H), 7.20-7.22 (m, 2H), 7.34-7.38 (m, 2H), 7.54 (dd, J = 8.0, 5.2 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 55.4, 109.8 (d, JCF = 26 Hz), 114.0, 114.4 (d, JCF = 23 Hz), 116.4 (d, JCF = 21 Hz), 122.7, 125.0 (d, JCF = 9 Hz), 126.6 (d, JCF = 3 Hz), 128.7 (d, JCF = 3 Hz), 130.6 (d, JCF = 9 Hz), 131.5, 133.6, 148.9 (d, JCF = 9 Hz), 150.6, 159.7, 162.3 (d, JCF = 249 Hz), 166.7 (d, JCF = 253 Hz), 195.2; HRMS (ESI) Calcd for C22H15F2O2 [M + H]+ 349.1040, found 349.1035.

2-(4-Methoxyphenyl)-6-methyl-3-(m-tolyl)-1H-inden-1-one (7l): The typical procedure was applied to (E)-4-methoxy-N-(3-methylbenzylidene)aniline (2f, 135.2 mg, 0.60 mmol) and 4-methoxybenzaldehyde (73 μL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 50/1) of the crude product afforded a mixture of the title compound and its minor regioisomer (2-(4-methoxyphenyl)-4-methyl-3-(m-tolyl)-1H-inden-1-one) as a dark red solid (67.1 mg, 66%). The ratio of the regioisomers was determined to be 2.7:1 by 1H NMR analysis. Rf 0.48 (hexane/EtOAc = 8/1); 1H NMR (400 MHz, CDCl3, major isomer): δ 2.36 (s, 3H), 2.37 (s, 3H), 3.79 (s, 3H), 6.81 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 7.10-7.16 (m, 2H), 7.17-7.26 (m, 3H), 7.28 (s, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.38 (s, 1H); 13C NMR (100 MHz,
CDCl₃): δ 21.5, 21.6, 55.3, 113.7 (two signals overlapping), 121.0, 123.5, 124.1, 125.8, 128.6, 129.0, 130.0, 131.2, 131.28, 131.33, 133.5, 138.6, 139.0, 143.0, 154.5, 159.2, 197.6; HRMS (ESI) Calcd for C₂₄H₂₁O₂ [M + H]+ 341.1542, found 341.1537.

2-(4-Methoxyphenyl)-7-methyl-3-(o-tolyl)-1H-inden-1-one (7m): The typical procedure was applied to (E)-4-methoxy-N-(2-methylbenzylidene)aniline (2g, 135.2 mg, 0.60 mmol) and 4-methoxybenzaldehyde (73 μL, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 100/1) of the crude product afforded the title compound as a light red oil (21.7 mg, 21%).

R₂ 0.45 (hexane/EtOAc = 10/1); ¹H NMR (400 MHz, CDCl₃): δ 2.09 (s, 3H), 2.64 (s, 3H), 3.78 (s, 3H), 6.62 (d, J = 7.2 Hz, 1H), 6.78 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 7.6 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.26-7.36 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 17.5, 20.1, 55.3, 113.8, 119.1, 124.1, 126.4, 126.9, 128.4, 128.8, 130.6, 131.0, 132.06, 132.14, 133.1, 133.4, 136.0, 137.8, 146.8, 153.4, 159.3, 198.5; HRMS (ESI) Calcd for C₂₄H₂₁O₂ [M + H]+ 341.1542, found 341.1537.

5-Methoxy-3-(4-methoxyphenyl)-2-(naphthalen-2-yl)-1H-inden-1-one (7n): The typical procedure was applied to (E)-4-methoxy-N-(4-methoxybenzylidene)aniline (2d, 144.8 mg, 0.60 mmol) and 2-naphthaldehyde (93.7 mg, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 10/1 – 5/1) of the crude product afforded the title compound as a red solid (84.2 mg, 72%).
m.p. 59.6-60.8 °C; R₂ 0.18 (hexane/EtOAc = 10/1); ¹H NMR (400 MHz, CDCl₃): δ 3.83 (s, 3H), 3.85 (s, 3H), 6.69 (dd, J = 8.0, 2.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 6.90 (app.d, J = 8.8 Hz, 2H), 7.23 (dd, J = 8.4, 2.0 Hz, 1H), 7.35 (app.d, J = 8.8 Hz, 2H), 7.44-7.47 (m, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.76-7.78 (m, 1H), 7.80-7.82 (m, 1H), 7.97 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 55.4, 55.9, 110.4, 110.7, 114.4, 124.0, 124.9, 125.0, 126.1, 126.4, 127.5, 127.6, 127.7, 128.6, 128.9, 129.9, 130.5, 132.8, 133.0, 133.4, 148.0, 153.4, 160.6, 164.5, 195.3; HRMS (ESI) Calcd for C₂₇H₂₃O₃ [M + H]+ 393.1491, found 393.1496.
Methyl 4-(5-methoxy-3-(4-methoxyphenyl)-1-oxo-1H-inden-2-yl)benzoate (7o): The typical procedure was applied to (E)-4-methoxy-N-(4-methoxybenzylidene)aniline (2d, 144.8 mg, 0.60 mmol) and methyl 4-formylbenzoate (98.5 mg, 0.60 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 10/1 – 3/1) of the crude product afforded the title compound as an orange solid (88.7 mg, 74%). m.p. 114.3–115.6 ºC; Rf 0.30 (hexane/EtOAc = 3/1); 1H NMR (400 MHz, CDCl3): δ 3.825 (s, 3H), 3.833 (s, 3H), 3.88 (s, 3H), 6.68 (dd, J = 8.0, 2.4 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 6.91 (app.d, J = 8.8 Hz, 2H), 7.27 (app.d, J = 8.8 Hz 2H), 7.35 (app.d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.92 (app.d, J = 8.4 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 52.2, 55.5, 55.9, 110.8, 111.0, 114.5, 123.8, 124.4, 125.0, 129.0, 129.4, 130.1, 130.3, 132.1, 136.3, 147.5, 154.8, 160.8, 164.5, 167.1, 194.6; HRMS (ESI) Calcd for C25H21O5 [M + H]+ 401.1389, found 401.1386.

2,2’-(1,3-Phenylene)bis(5-methyl-3-(p-tolyl)-1H-inden-1-one) (7p): In a Schlenk tube were placed CoBr2 (13.2 mg, 0.060 mmol), IPr•HCl (23.6 mg, 0.060 mmol), (E)-4-methoxy-N-(1-(p-tolyl)ethylidene)aniline (2c, 135.2 mg, 0.60 mmol), and THF (1.42 mL). To the mixture was added a THF solution of (CH3)3CCH2MgBr (0.68 M, 1.58 mL, 1.08 mmol) dropwise at 0 ºC. After stirring for 30 min, another portion of 2c (135.2 mg, 0.60 mmol) was added. The resulting mixture was stirred at room temperature for 12 h, followed by the addition of H2O (0.6 mL) and isophthalaldehyde (26.8 mg, 0.20 mmol). After stirring for 1 h, aq. HCl (3 M, 2 mL) was added, and the resulting mixture was stirred at 100 ºC for 12 h. The reaction was cooled to room temperature, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over MgSO4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc = 3/1) to afford the title compound as a dark red solid (75.3 mg, 69% based on isophthalaldehyde). m.p. 193.4–194.5 ºC; Rf 0.15 (hexane/EtOAc = 10/1); 1H NMR (400 MHz, CDCl3): δ 2.34 (s, 6H), 2.40 (s, 6H), 7.00 (s, 2H), 7.06 (d, J = 7.2 Hz, 2H), 7.09-7.12 (m, 3H), 7.21-7.26 (m, 8H), 7.32 (s, 1H), 7.44 (d, J = 7.2 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 21.7, 22.3, 122.7, 123.1,
127.9, 128.7 (two signals overlapping), 129.0, 129.4, 129.6, 129.9, 131.2, 131.8, 132.6, 139.5, 144.3, 145.9, 155.3, 196.2; HRMS (ESI) Calcd for C_{40}H_{31}O_{2} [M + H]^+ 543.2324, found 543.2325.

1-(2-Benzoylphenyl)-3,3-dimethylbutan-1-one (7q): The typical procedure was applied to (E)-N-benzylidene-4-methoxyaniline (2b, 63.4 mg, 0.30 mmol) and pivalaldehyde (65 µL, 0.6 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 20/1–5/1) of the crude product afforded the title compound as a red oil (39.0 mg, 46%).

R_f 0.20 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.94 (s, 9H), 2.75 (s, 2H), 7.39-7.42 (m, 3H), 7.50-7.54 (m, 1H), 7.55-7.59 (m, 2H), 7.72-7.74 (m, 2H), 7.82-7.84 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 29.8, 31.7, 51.5, 128.5, 128.7, 129.0, 129.6, 129.8, 131.7, 133.0, 137.6, 139.9, 141.0, 198.0, 201.3; HRMS (ESI) Calcd for C_{19}H_{21}O_{2} [M + H]^+ 281.1542, found 281.1545.
Proposed Mechanism for the Formation of Indenone

Below is shown a possible mechanism for the formation of indene, which is similar to that proposed for the reaction of isobenzofuran and benzaldehyde by Kuninobu and Takai.\(^6\) Formation of the diketone product 7q from pivalaldehyde can be explained by hydrolysis of the intermediate A.

Scheme S1. Proposed mechanism for the condensation of isoindole and aldehyde

NMR Spectra

3a
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3m

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3n

\[ \text{1H NMR CDCl3 400MHz, BRFP1} \]

\[ \text{13C NMR CDCl3 400MHz, BRFP1} \]

S35
3p

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7a

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