Supplementary Information

Pivalophenone N–H Imine as a Benzonitrile Surrogate for Directed C–H Bond Functionalization

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Electronic Supplementary Material (ESI) for Chemical Science.
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Material and Methods

**General.** All reactions dealing with air- and moisture-sensitive compounds were carried out in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash column chromatography was performed using 40-63µm silica gel (Si 60, Merck). $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA-400 (400 MHz), Bruker AV-300 (300 MHz), or AV-400 (400 MHz) NMR spectrometers. $^1$H and $^{13}$C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm), and $^{31}$P NMR spectra are reported in reference to an external standard, 85% phosphoric acid (0 ppm). Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 system equipped with glass capillary column DB-5 (Agilent J&W, 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 determined using a capillary melting point apparatus and are uncorrected.

**Materials.** Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. THF was distilled over Na/benzophenone. Grignard reagents were prepared from the corresponding alkyl halides and magnesium turnings in THF, and titrated before use. CoBr$_2$ (99%) was purchased from Sigma-Aldrich and used as received. Co(acac)$_3$ was purchased from Alfa Aesar and used as received. $N,N$-Diisopropylimidazolinium tetrafluoroborate ($\textbf{L1}$) was purchased from Sigma-Aldrich and used as received.
Preparation of Starting Materials and Ligand

Pivalophenone N–H Imines

All imines shown below were synthesized from the corresponding aryl nitriles and t-BuLi according to the literature procedures, and purified by recrystallization or distillation. Spectral data for 1a, 1d, 1f, and 1g showed good agreement with the literature data.

2,2-Dimethyl-1-(p-tolyl)propan-1-imine (1b): Light yellow liquid; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.13 (brs, 1H), 7.14 – 7.08 (m, 4H), 2.35 (s, 3H), 1.23 (s, 9H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.5, 139.7, 137.8, 128.7, 126.5, 40.2, 28.7, 21.3; HRMS (ESI) Calcd for C\(_{12}\)H\(_{18}\)N [M + H]\(^+\) 176.1439, found 176.1435.

1-[(1,1'-Biphenyl]-4-yl)-2,2-dimethylpropan-1-imine (1c): White solid; M.p. 92-93 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.27 (brs, 1H), 7.62 – 7.56 (m, 4H), 7.48 – 7.42 (m, 2H), 7.39 – 7.34 (m, 1H), 7.30 (d, \(J = 8.0\) Hz, 2H), 1.30 (s, 9H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.2, 141.0, 140.6, 129.0 (two signals overlapped), 127.7, 127.2, 127.1, 126.8, 28.6; HRMS (ESI) Calcd for
C_{17}H_{20}N [M + H]^+ 238.1596, found 238.1586.

2,2-Dimethyl-1-(4-(trifluoromethoxy)phenyl)propan-1-imine (1e): Light yellow liquid; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.16 (brs, 1H), 7.28 – 7.17 (m, 4H), 1.23 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 189.1, 149.1, 141.0, 128.3, 120.7, 120.6 (q, \(^{1}\)J\(_{C-F}\) = 257.5 Hz), 40.5, 28.5; HRMS (ESI) Calcd for C\(_{12}\)H\(_{15}\)NOF \([M + H]^+\) 246.1106, found 246.1105.

\[
\begin{align*}
\text{F}_3\text{CO} & \quad \text{NH} \\
& \quad \text{F} \\
\end{align*}
\]

\(\text{1-HNMe}_2\) \(-\text{methyl}-1-(4\text{-fluorophenyl})\text{propan-1-imine (1h): Light yellow liquid; \(^{1}\)H NMR (400 MHz, CDCl}\(_3\)): \(\delta\) 9.12 (brs, 1H), 7.14 (brs, 2H), 6.99 – 6.94 (m, 2H), 1.18 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 189.4, 162.4 (d, \(^{1}\)J\(_{C-F}\) = 247.2 Hz), 138.4, 128.3, 115.0 (d, \(^{2}\)J\(_{C-F}\) = 21.4 Hz), 40.5, 28.4; HRMS (ESI) Calcd for C\(_{11}\)H\(_{15}\)NF \([M + H]^+\) 180.1189, found 180.1196.

\[
\begin{align*}
\text{Me} & \quad \text{NH} \\
& \quad \text{F} \\
\end{align*}
\]

2,2-Dimethyl-1-(\(m\)-tolyl)propan-1-imine (1i): Light yellow liquid; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.13 (brs, 1H), 7.19 (t, \(J = 7.9\) Hz, 1H), 7.12 (d, \(J = 7.3\) Hz, 1H), 6.99 – 6.95 (m, 2H), 2.34 (s, 3H), 1.22 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.4, 142.4, 137.7, 128.7, 127.8, 127.1, 123.5, 40.1, 28.6, 21.5; HRMS (ESI) Calcd for C\(_{12}\)H\(_{16}\)N \([M + H]^+\) 176.1439, found 176.1437.

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{NH} \\
& \quad \text{F} \\
\end{align*}
\]

2,2-Dimethyl-1-(3-(trifluoromethyl)phenyl)propan-1-imine (1j): Light yellow liquid; \(^{1}\)H
NMR (400 MHz, CDCl₃): δ 9.20 (brs, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.52 – 7.33 (m, 3H), 1.21 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 188.8, 143.0, 130.6 (q, ²J_C-F = 32.1 Hz), 129.9, 128.7, 124.9 (q, ³J_C-F = 3.8 Hz), 124.0 (q, ⁴J_C-F = 272.2 Hz), 123.3, 40.4, 28.3; HRMS (ESI) Calcd for C₁₂H₁₅NF₃ [M + H]⁺ 230.1157, found 230.1161.

NHMeO

1-(3-Methoxyphenyl)-2,2-dimethylpropan-1-imine (1k): Light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 9.18 (brs, 1H), 7.25 (t, J = 8.3 Hz, 1H), 6.87 (dd, J = 8.3, 2.3 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.73 (s, 1H), 3.81 (s, 3H), 1.24 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 188.2, 159.2, 143.7, 129.3, 119.0, 113.4, 112.6, 55.4, 40.9, 28.7; HRMS (ESI) Calcd for C₁₂H₁₈NO [M + H]⁺ 192.1389, found 192.1388.

O

1-(Benzo[d][1,3]dioxol-5-yl)-2,2-dimethylpropan-1-imine (1l): Light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 9.13 (brs, 1H), 6.75 – 6.71 (m, 1H), 6.65 (d, J = 7.8 Hz, 1H), 5.92 (s, 2H), 1.19 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 189.5, 147.4, 147.1, 136.2, 120.3, 108.0, 107.5, 101.2, 40.3, 28.7; HRMS (ESI) Calcd for C₁₂H₁₆NO₂ [M + H]⁺ 206.1181, found 206.1182.

NH

2,2-Dimethyl-1-(naphthalen-2-yl)propan-1-imine (1m): Light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 9.35 (brs, 1H), 7.86 – 7.80 (m, 3H), 7.68 (s, 1H), 7.54 – 7.48 (m, 2H), 7.35 (d, J = 8.1 Hz, 1H), 1.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 190.3, 145.8, 139.9, 132.8, 128.3, 127.8, 127.7, 126.6, 126.5, 125.4, 124.8, 40.4, 28.7; HRMS (ESI) Calcd for C₁₅H₁₈N [M + H]⁺ 212.1439, found 212.1447.
1-(3,5-Difluorophenyl)-2,2-dimethylpropan-1-imine (1n): Light yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.17 (brs, 1H), 6.89 – 6.58 (m, 3H), 1.19 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 188.0, 162.6 (dd, $^1J_{C-F} = 250.1$ Hz, $^3J_{C-F} = 12.5$ Hz), 145.3 (d, $^3J_{C-F} = 15.4$ Hz), 110.3, 103.6 (t, $^2J_{C-F} = 25.0$ Hz), 40.2, 28.4; HRMS (ESI) Calcd for C$_{11}$H$_{14}$NF$_2$ [M + H]$^+$ 198.1094, found 198.1096.

Preparation of L$_2$•HBr

(E)-N,N'-Bis(2,6-diethylphenyl)formamidine: The formamidine was prepared as follows according to the method described by Grubbs et al.$^4$ A mixture of 2,6-diethylaniline (8.95 g, 60 mmol, 2 equiv), triethylorthoformate (4.45 g, 30 mmol, 1 equiv), and glacial acetic acid (0.1 mL, 1.5 mmol, 0.05 equiv) was heated at 140 °C overnight. The crude solid was triturated, washed with cold n-pentane, and filtered through a glass frit. The solid was dried under the reduced pressure to give the title compound as a pale yellow solid (4.62 g, 50%). The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^5$

1,3-Bis-(2,6-diethylphenyl)-4,5,6,7-tetrahydro-3H-benzoimidazol-1-ium bromide (L$_2$•HBr): The synthesis was performed according to the procedure reported by Glorius and coworkers.$^6$ To a suspension of $N,N'$-bis(2,6-diethylphenyl)formamidine (1.39 g, 4.5 mmol, 1 equiv) in
acetonitrile (9 mL) were added diisopropylethylamine (0.90 mL, 5.4 mmol, 1.2 equiv) and 2-bromocyclohexanone (1.59 g, 9.0 mmol, 2 equiv). The resulting mixture was stirred at 110 °C for 20 h. The reaction progress was monitored by TLC (CH$_2$Cl$_2$/MeOH 10:1). After full consumption of the formamidine, the volatiles were removed under reduced pressure. The residue was suspended in toluene (11 mL), followed by the addition of acetic anhydride (1.30 mL, 13.5 mmol, 3 equiv) and 48% HBr in acetic acid (0.77 mL, 6.8 mmol, 1.5 equiv). The resulting mixture was stirred at 90 °C for 24 h. The mixture was then transferred into a separatory funnel containing CH$_2$Cl$_2$ and H$_2$O (50 mL each). After separation of the two layers, the aqueous layer was extracted with CH$_2$Cl$_2$ (50 mL x 3). The combined organic extracts were dried over anhydrous MgSO$_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: CH$_2$Cl$_2$/MeOH = 100/1 to 10/1). The collected solids were dried under vacuum and then dissolved in hot acetonitrile. The solution was stirred vigorously with charcoal powder for 5 min, followed by filtration and recrystallization from CH$_2$Cl$_2$/Et$_2$O to afford the title compound as a white powder (589 mg, 28%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.78–10.68 (m, 1H), 7.48 (t, $J$ = 7.7 Hz, 2H), 7.29 (d, $J$ = 7.7 Hz, 4H), 2.48–2.37 (m, 8H), 2.31 (brs, 4H), 1.92 (brs, 4H), 1.23–1.19 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.6, 137.7, 131.8, 131.2, 130.0, 127.6, 24.5, 21.8, 20.4, 14.6; HRMS (ESI) Calcd for C$_{27}$H$_{36}$N$_2$Br [M + H]$^+$ 467.2062, found 467.2066.
Cobalt-Catalyzed ortho-Alkylation of Pivalophenone N–H Imines with Alkyl Bromides

Table S1. Screening of Reaction Conditions

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<th>entry</th>
<th>ligand (mol%)</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
<td>1</td>
<td>PPh₃ (20)</td>
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<tr>
<td>2</td>
<td>PCy₃ (20)</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>dppe (10)</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>IMes•HCl (10)</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>IPr•HCl (10)</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>SIMes•HCl (10)</td>
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<tr>
<td>7</td>
<td>SIPr•HCl (10)</td>
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</tr>
<tr>
<td>8</td>
<td>L₁•HBF₄ (10)</td>
<td>90&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>L₃•HBF₄ (10)</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>L₄•HBr (10)</td>
<td>76</td>
</tr>
<tr>
<td>11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>L₁•HBF₄ (10)</td>
<td>55</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined by GC using <i>n</i>-tridecane as an internal standard.  
<sup>b</sup> Isolated yield.  
<sup>c</sup> <i>n</i>-Octyl chloride was used instead of <i>n</i>-octyl bromide.
**General Procedure: 2,2-Dimethyl-1-(2-octylphenyl)propan-1-imine (3aa).** In a Schlenk tube were placed L1•HBF$_4$ (4.9 mg, 0.020 mmol), a freshly prepared THF solution of CoBr$_2$ (0.20 M, 0.10 mL, 0.020 mmol), and THF (0.3 mL). The resulting solution was cooled in an ice bath, followed by the addition of t-BuCH$_2$MgBr (2.0 M in THF, 0.20 mL, 0.40 mmol). After stirring for 30 min, 2,2-dimethyl-1-phenylpropan-1-imine (1a, 33 mg, 0.20 mmol) and 1-bromoocotane (2a, 52 µL, 0.30 mmol) were added sequentially. The resulting mixture was warmed to room temperature and stirred for 12 h, and then filtered through a short pad of silica gel, which was washed with ethyl acetate (5 mL). The filtrate was concentrated under reduced pressure. Silica gel chromatography (eluent: hexane/EtOAc/NEt$_3$ = 100/1/1) of the crude product afforded the title compound as a colorless oil (49 mg, 90%).

$R_f$ 0.60 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.19 (brs, 1H), 7.26 – 7.23 (m, 2H), 7.15 – 7.10 (m, 1H), 7.01 (d, $J$ = 7.5 Hz, 1H), 2.48 – 2.44 (m, 2H), 1.60 – 1.52 (m, 2H), 1.37 – 1.20 (m, 19H), 0.87 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.9, 141.6, 139.0, 129.4, 127.9, 126.2, 125.1, 40.6, 33.9, 32.1, 32.0, 30.0, 29.7, 29.5, 28.9, 22.9, 14.3; HRMS (ESI) Calcd for C$_{19}$H$_{32}$N [M + H]$^+$ 274.2535, found 274.2535.

**2,2-Dimethyl-1-(2-phenethylphenyl)propan-1-imine (3ab):** Light yellow oil (44 mg, 83%); $R_f$ 0.51 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.96 (s, 1H), 7.35 – 7.25 (m, 4H), 7.22 – 7.11 (m, 4H), 7.02 (d, $J$ = 7.6 Hz, 1H), 2.91 – 2.87 (m, 2H), 2.80 – 2.76 (m, 2H), 1.21 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.4, 141.7, 137.7, 136.1, 129.5, 128.7 (two signals overlapped), 128.0, 126.4, 126.3, 125.5, 40.6, 38.3, 36.1, 28.9; HRMS (ESI) Calcd for C$_{19}$H$_{24}$N [M + H]$^+$ 266.1909, found 266.1908.

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2,2-Dimethyl-1-(2-(3-phenylpropyl)phenyl)propan-1-imine (3ac): Light yellow oil (51 mg, 91%); $R_f$ 0.50 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.20 (brs, 1H), 7.31 – 7.23 (m, 4H), 7.20 – 7.11 (m, 4H), 7.01 (d, $J = 7.5$ Hz, 1H), 2.67 (t, $J = 7.6$ Hz, 2H), 2.53 – 2.49 (m, 2H), 1.97 – 1.87 (m, 2H), 1.18 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.7, 142.1, 141.6, 138.4, 129.3, 128.7, 128.6, 128.0, 126.3, 126.0, 125.3, 40.6, 36.2, 33.44 (two signals overlapped), 28.8; HRMS (ESI) Calcd for C$_{20}$H$_{26}$N [M + H]$^+$ 280.2065, found 280.2065.

1-(2-(4-Chlorobutyl)phenyl)-2,2-dimethylpropan-1-imine (3ad): Light yellow oil (38 mg, 75%); $R_f$ 0.49 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.07 (brs, 1H), 7.27 – 7.23 (m, 2H), 7.19 – 7.12 (m, 1H), 7.03 (d, $J = 7.6$ Hz, 1H), 3.54 (t, $J = 6.4$ Hz, 2H), 2.54 – 2.48 (m, 2H), 1.86 – 1.65 (m, 4H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.7, 142.1, 141.6, 138.4, 129.3, 128.7, 128.6, 128.0, 126.3, 126.0, 125.3, 40.6, 36.2, 33.44 (two signals overlapped), 28.8; HRMS (ESI) Calcd for C$_{15}$H$_{23}$NCl [M + H]$^+$ 252.1519, found 252.1517.

1-(2-(4-Fluorobutyl)phenyl)-2,2-dimethylpropan-1-imine (3ae): Light yellow oil (38 mg, 80%); $R_f$ 0.50 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.09 (brs, 1H), 7.26 – 7.25 (m, 2H), 7.19 – 7.12 (m, 1H), 7.03 (d, $J = 7.7$ Hz, 1H), 4.53 – 4.49 (m, 1H), 4.40 – 4.38 (m, 1H), 2.55 – 2.51 (m, 2H), 1.80 – 1.65 (m, 4H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.8, 141.4, 138.1, 129.3, 128.1, 126.4, 125.4, 84.1 (d, $^1$J$_{C-F}$ = 164.8 Hz), 40.7, 33.4, 30.6 (d, $^2$J$_{C-F}$ = 19.6 Hz), 28.9, 27.5 (d, $^3$J$_{C-F}$ = 4.7 Hz); HRMS (ESI) Calcd for C$_{15}$H$_{23}$NF [M + H]$^+$ 236.1815, found 236.1811.
2,2-Dimethyl-1-(2-(pent-4-en-1-yl)phenyl)propan-1-imine (3af): Light yellow oil (38 mg, 82%); $R_f$ 0.62 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.18 (brs, 1H), 7.28 – 7.21 (m, 2H), 7.16 – 7.11 (m, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 5.86 – 5.75 (m, 1H), 5.06 – 4.94 (m, 2H), 2.51 – 2.46 (m, 2H), 2.12 – 2.07 (m, 2H), 1.72 – 1.64 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.8, 141.6, 138.5 (two signals overlapped), 129.4, 128.0, 126.3, 125.2, 115.2, 40.6, 34.0, 33.3, 31.0, 28.9; HRMS (ESI) Calcd for C$_{16}$H$_{24}$N [M + H]$^+$ 230.1909, found 230.1911.

1-(2-(Hex-5-en-1-yl)phenyl)-2,2-dimethylpropan-1-imine (3ag): Light yellow oil (34 mg, 70%); $R_f$ 0.65 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.10 (brs, 1H), 7.27 – 7.22 (m, 2H), 7.17 – 7.17 (m, 1H), 7.01 (d, $J = 7.7$ Hz, 1H), 5.85 – 5.74 (m, 1H), 5.03 – 4.91 (m, 2H), 2.52 – 2.43 (m, 2H), 2.10 – 2.03 (m, 2H), 1.65 – 1.55 (m, 2H), 1.47 – 1.39 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.8, 141.6, 138.9, 138.7, 129.4, 128.0, 126.2, 125.2, 114.8, 40.6, 39.9, 33.8 (two signals overlapped), 31.4, 28.9; HRMS (ESI) Calcd for C$_{17}$H$_{26}$N [M + H]$^+$ 244.2065, found 244.2067.

2,2-Dimethyl-1-(2-(4-methylpent-3-en-1-yl)phenyl)propan-1-imine (3ah): Light yellow oil (37 mg, 75%); $R_f$ 0.50 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.14 (brs, 1H), 7.30 – 7.22 (m, 2H), 7.17 – 7.11 (m, 1H), 7.01 (d, $J = 7.3$ Hz, 1H), 5.17 – 5.10 (m, 1H), 2.52 – 2.48 (m, 2H), 2.28 – 2.22 (m, 2H), 1.68 (s, 3H), 1.55 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.7, 141.6, 138.4, 132.8, 129.5, 127.9, 126.2, 125.2, 123.8, 40.6, 34.0, 30.4, 28.9, 25.9, 17.9; HRMS (ESI) Calcd for C$_{17}$H$_{26}$N [M + H]$^+$ 244.2065, found 244.2070.
1-(2-Isobutylphenyl)-2,2-dimethylpropan-1-imine (3ai): Light yellow oil (35 mg, 81%); $R_f$ 0.62 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.16 (brs, 1H), 7.26 – 7.20 (m, 2H), 7.14 (t, $J = 7.2$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 2.36 (d, $J = 7.3$ Hz, 2H), 1.95 – 1.87 (m, 1H), 1.21 (s, 9H), 0.88 (d, $J = 6.5$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.0, 142.1, 137.6, 129.8, 127.8, 126.3, 125.2, 43.0, 40.6, 30.0, 29.0, 22.7; HRMS (ESI) Calcd for C$_{15}$H$_{24}$N $[M + H]^+$ 218.1909, found 218.1914.

1-(2-(Cyclobutylmethyl)phenyl)-2,2-dimethylpropan-1-imine (3aj): Light yellow oil (41 mg, 90%); $R_f$ 0.63 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.12 (brs, 1H), 7.25 – 7.17 (m, 2H), 7.13 (td, $J = 7.3$, 1.8 Hz, 1H), 7.00 (d, $J = 7.4$ Hz, 1H), 2.62 – 2.50 (m, 3H), 2.09 – 2.00 (m, 2H), 1.89 – 1.64 (m, 4H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.9, 141.7, 137.3, 129.1, 127.8, 126.2, 125.2, 40.6 (two signals overlapped), 37.1, 28.9 (two signals overlapped), 18.6; HRMS (ESI) Calcd for C$_{16}$H$_{24}$N $[M + H]^+$ 230.1909, found 230.1915.

1-(2-(Cyclohexylmethyl)phenyl)-2,2-dimethylpropan-1-imine (3ak): Light yellow oil (45 mg, 87%); $R_f$ 0.64 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.13 (brs, 1H), 7.25 – 7.19 (m, 2H), 7.13 (td, $J = 7.2$, 2.0 Hz, 1H), 7.00 (d, $J = 7.6$ Hz, 1H), 2.36 (d, $J = 7.1$ Hz,
2H), 1.72 – 1.49 (m, 6H), 1.26 – 1.10 (m, 12H), 0.98 – 0.85 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.0, 142.1, 137.2, 129.9, 127.6, 126.2, 125.1, 41.7, 40.6, 39.6, 33.5, 29.0, 26.7, 26.6; HRMS (ESI) Calcd for C$_{18}$H$_{28}$N [M + H]$^+$ 258.2222, found 258.2222.

![Image](https://via.placeholder.com/150)

2,2-Dimethyl-1-(2-neopentylphenyl)propan-1-imine (3a): Light yellow oil (42 mg, 91%); $R_f$ 0.67 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.26 (brs, 1H), 7.28 – 7.20 (m, 2H), 7.16 (td, $J = 7.3, 1.7$ Hz, 1H), 6.97 (d, $J = 7.3$ Hz, 1H), 2.43 (s, 2H), 1.17 (s, 9H), 0.92 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.9, 142.6, 135.8, 130.9, 127.1, 126.7, 125.7, 47.4, 40.7, 32.8, 30.3, 29.2; HRMS (ESI) Calcd for C$_{16}$H$_{26}$N [M + H]$^+$ 232.2058.

![Image](https://via.placeholder.com/150)

1-(2-Cyclopentylphenyl)-2,2-dimethylpropan-1-imine (3am): Light yellow oil (39 mg, 85%); $R_f$ 0.56 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.11 (s, 1H), 7.34 – 7.25 (m, 2H), 7.11 (td, $J = 7.5, 1.4$ Hz, 1H), 6.99 (dd, $J = 7.6, 1.2$ Hz, 1H), 2.85 – 2.73 (m, 1H), 2.03 – 1.92 (m, 2H), 1.87 – 1.76 (m, 2H), 1.70 – 1.50 (m, 4H), 1.23 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.1, 143.5, 141.6, 128.3, 126.9, 125.9, 124.9, 43.4, 40.6, 28.9 (two signals overlapped), 26.4; HRMS (ESI) Calcd for C$_{16}$H$_{24}$N [M + H]$^+$ 230.1901, found 230.1901.

![Image](https://via.placeholder.com/150)

1-(2-Cyclohexylphenyl)-2,2-dimethylpropan-1-imine (3an): Light yellow oil (42 mg, 87%); $R_f$ 0.56 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.13 (brs, 1H), 7.32 – 7.24...
(m, 2H), 7.14 – 7.10 (m, 1H), 7.00 – 6.96 (m, 1H), 2.36 (tt, \(J = 11.7, 3.1\) Hz, 1H), 1.86 – 1.65 (m, 6H), 1.37 – 1.19 (m, 13H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.1, 144.0, 141.0, 128.1, 127.0, 126.2, 125.2, 42.3, 40.6, 29.0, 27.1 (two signals overlapped), 26.3; HRMS (ESI) Calcd for C\(_{17}\)H\(_{26}\)N [M + H]\(^+\) 244.2065, found 244.2070.

![Diagram](attachment:image)

**1-(2-Cycloheptylphenyl)-2,2-dimethylpropan-1-imine (3ao):** Light yellow oil (43 mg, 84%); \(R_f\) 0.56 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.14 (brs, 1H), 7.27 – 7.26 (m, 2H), 7.14 – 7.07 (m, 1H), 6.97 (d, \(J = 7.7\) Hz, 1H), 2.52 (t, \(J = 10.1\) Hz, 1H), 1.85 – 1.41 (m, 12H), 1.23 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.2, 146.3, 142.6, 128.3, 126.0, 124.9, 43.7, 40.6, 29.0, 28.0 (two signals overlapped), 27.7; HRMS (ESI) Calcd for C\(_{18}\)H\(_{28}\)N [M + H]\(^+\) 258.2222, found 258.2228.

![Diagram](attachment:image)

**1-(2-Isopropylphenyl)-2,2-dimethylpropan-1-imine (3ap):** Light yellow oil (21 mg, 51%); \(R_f\) 0.62 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.17 (brs, 1H), 7.34 – 7.27 (m, 2H), 7.13 (td, \(J = 7.6, 1.5\) Hz, 1H), 6.99 (dd, \(J = 7.6, 0.8\) Hz, 1H), 2.78 (hept, \(J = 6.9\) Hz, 1H), 1.27 – 1.18 (m, 15H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.0, 145.2, 140.7, 128.3, 126.2 (two signals overlapped), 125.2, 47.4, 40.7, 31.4, 28.9; HRMS (ESI) Calcd for C\(_{14}\)H\(_{22}\)N [M + H]\(^+\) 204.1752, found 204.1757.

![Diagram](attachment:image)

**1-(2-(sec-Butyl)phenyl)-2,2-dimethylpropan-1-imine (3aq):** Light yellow oil (24 mg, 53%); \(R_f\)
0.59 (hexane/EtOAc/NEt₃ = 10/1/1); ¹H NMR (400 MHz, CDCl₃): δ 9.14 (brs, 1H), 7.31 – 7.25 (m, 2H), 7.16 – 7.10 (m, 1H), 6.99 (d, J = 7.6 Hz, 1H), 2.56 – 2.43 (m, 1H), 1.58 (d, J = 6.5 Hz, 2H), 1.23 (s, 9H), 1.19 (d, J = 7.0 Hz, 3H), 0.85 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 191.0, 144.3, 141.3, 128.2, 126.4, 126.2, 125.1, 40.6, 38.2, 30.4, 29.2, 29.1, 22.2, 12.6; HRMS (ESI) Calcd for C₁₅H₂₄N [M + H]⁺ 218.1909, found 218.1904.

2,2-dimethyl-1-(4-methyl-2-octylphenyl)propan-1-imine (3ba): Light yellow oil (50 mg, 87%); Rᵥ 0.62 (hexane/EtOAc/NEt₃ = 10/1/1); ¹H NMR (400 MHz, CDCl₃): δ 9.09 (brs, 1H), 7.05 (s, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 2.45 – 2.38 (m, 2H), 2.32 (s, 3H), 1.60 – 1.50 (m, 2H), 1.38 – 1.18 (m, 19H), 0.89 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 191.0, 138.9 (two signals overlapped), 137.5, 130.0, 126.1, 125.8, 40.6, 33.9, 32.1, 30.1, 29.7, 29.5, 28.97, 22.9, 21.4, 14.3; HRMS (ESI) Calcd for C₂₀H₃₄N [M + H]⁺ 288.2691, found 288.2700.

2,2-Dimethyl-1-(3-octyl-[1,1'-biphenyl]-4-yl)propan-1-imine (3ca): Light yellow oil (60 mg, 87%); Rᵥ 0.57 (hexane/EtOAc/NEt₃ = 10/1/1); ¹H NMR (400 MHz, CDCl₃): δ 9.27 (brs, 1H), 7.62 – 7.58 (m, 2H), 7.50 – 7.42 (m, 3H), 7.39 – 7.33 (m, 2H), 7.10 (d, J = 7.9 Hz, 1H), 2.57 – 2.51 (m, 1H), 1.69 – 1.59 (m, 1H), 1.42 – 1.22 (m, 19H), 0.89 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 190.7, 141.0 (two signals overlapped), 140.8, 139.5, 129.0, 128.1, 127.6, 127.3, 126.7, 123.9, 40.7, 34.1, 32.1, 30.1, 29.7, 29.4, 29.0, 22.9 (two signals overlapped), 14.3; HRMS (ESI) Calcd for C₂₅H₃₆N [M + H]⁺ 350.2848, found 350.2856.
**2,2-Dimethyl-1-(3-octyl-[1,1'-biphenyl]-4-yl)propan-1-imine (3da):** Light yellow oil (60 mg, 87%); $R_f$ 0.50 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.05 (brs, 1H), 6.93 (d, $J$ = 8.4 Hz, 1H), 6.77 (d, $J$ = 2.5 Hz, 1H), 6.67 (dd, $J$ = 8.4, 2.6 Hz, 1H), 3.79 (s, 3H), 2.46 – 2.39 (m, 2H), 1.61 – 1.51 (m, 2H), 1.34 – 1.18 (m, 19H), 0.87 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.7, 159.1, 140.8, 131.2, 127.3, 114.7, 110.4, 55.4, 40.7, 34.1, 32.1, 31.9, 30.0, 29.7, 29.4, 28.9, 22.9, 14.3; HRMS (ESI) Calcd for C$_{20}$H$_{34}$NO [M + H]$^+$ 304.2640, found 304.2640.

**2,2-Dimethyl-1-(2-octyl-4-(trifluoromethoxy)phenyl)propan-1-imine (3ea):** Light yellow oil (63 mg, 88%); $R_f$ 0.52 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.20 (brs, 1H), 7.09 (s, 1H), 7.05 – 6.97 (m, 2H), 2.50 – 2.43 (m, 2H), 1.62 – 1.51 (m, 2H), 1.37 – 1.15 (m, 19H), 0.87 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.7, 148.9, 141.7, 140.0, 127.6, 121.6, 120.7 (q, $^1$J$_{C-F}$ = 120.71 Hz), 117.6, 40.7, 33.8, 32.1, 31.6, 29.9, 29.6, 29.4, 28.8, 22.9, 14.3; HRMS (ESI) Calcd for C$_{20}$H$_{31}$NOF$_3$ [M + H]$^+$ 358.2358, found 358.2355.

**2,2-Dimethyl-1-(4-(methylthio)-2-octylphenyl)propan-1-imine (3fa):** Light yellow oil (51 mg, 88%); $R_f$ 0.60 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.15 (brs, 1H), 7.13 (d, $J$ = 1.6 Hz, 1H), 7.02 (dd, $J$ = 8.0, 1.8 Hz, 1H), 6.93 (d, $J$ = 8.0 Hz, 1H), 2.48 (s, 3H), 2.45 – 2.39 (m, 2H), 1.59 – 1.51 (m, 2H), 1.37 – 1.18 (m, 19H), 0.87 (t, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.4, 139.8, 138.5, 138.0, 127.4, 126.7, 123.1, 40.7, 33.9, 32.1, 31.9, 30.0, 29.6, 29.4, 28.9, 22.9, 15.9, 14.3; HRMS (ESI) Calcd for C$_{20}$H$_{34}$NS [M + H]$^+$ 320.2412, found 320.2411.
1-(4-(Dimethylamino)-2-octylphenyl)-2,2-dimethylpropan-1-one (3ga): The crude reaction mixture was hydrolyzed with HCl (3 M, 1 mL). The mixture was neutralized and extracted with ethyl acetate. The extracts were concentrated under reduced pressure, and the residue was subjected to silica gel chromatography (eluent: hexane/EtOAc = 50/1) to afford the title compound as a light yellow oil (52 mg, 82%).

\[ R_f 0.55 \text{ (hexane/EtOAc = 10/1); } ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta 7.20 (d, J = 8.6 \text{ Hz}, 1\text{H}), 6.54 (d, J = 2.6 \text{ Hz}, 1\text{H}), 6.48 (dd, J = 8.6, 2.6 \text{ Hz}, 1\text{H}), 2.97 (s, 6\text{H}), 2.53 – 2.47 (m, 2\text{H}), 1.61 – 1.51 (m, 2\text{H}), 1.37 – 1.22 (m, 19\text{H}), 0.91 – 0.85 (m, 3\text{H}); ^13C \text{ NMR (100 MHz, CDCl}_3\text{): } \delta 213.8, 150.9, 142.4, 128.5, 127.2, 113.6, 108.4, 45.0, 40.5, 34.6, 32.4, 32.2, 30.1, 29.8, 29.5, 28.4, 22.9, 14.4, 1.3; HRMS (ESI) Calcd for C\textsubscript{21}H\textsubscript{35}NO [M + H]\textsuperscript{+} 317.2719, found 317.2721. \]

1-(4-Fluoro-2-octylphenyl)-2,2-dimethylpropan-1-imine (3ha): Light yellow oil (50 mg, 85%); \[ R_f 0.58 \text{ (hexane/EtOAc/NEt}_3\text{ = 10/1/1); } ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta 8.96 (brs, 1\text{H}), 7.01 – 6.91 (m, 2\text{H}), 6.86 – 6.79 (m, 1\text{H}), 2.48 – 2.41 (m, 2\text{H}), 1.60 – 1.51 (m, 2\text{H}), 1.36 – 1.17 (m, 19\text{H}), 0.89 – 0.85 (m, 3\text{H}); ^13C \text{ NMR (100 MHz, CDCl}_3\text{): } \delta 190.0, 162.4 (d, ^1J_{C,F} = 246.0 \text{ Hz}), 141.9, 137.4, 127.8 (d, ^2J_{C,F} = 8.0 \text{ Hz}), 115.8 (d, ^2J_{C,F} = 21.0 \text{ Hz}), 112.2 (d, ^2J_{C,F} = 21.5 \text{ Hz}), 40.7, 33.9, 32.1, 31.5, 29.9, 29.6, 29.4, 28.8, 22.9, 14.3; HRMS (ESI) Calcd for C\textsubscript{19}H\textsubscript{31}NF [M + H]\textsuperscript{+} 292.2441, found 292.2444. \]

2,2-Dimethyl-1-(5-methyl-2-octylphenyl)propan-1-imine (3ia): Light yellow oil (50 mg, 86%); \[ R_f 0.61 \text{ (hexane/EtOAc/NEt}_3\text{ = 10/1/1); } ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta 8.89 (brs, 1\text{H}), \]
7.13 (d, J = 7.9 Hz, 1H), 7.05 (dd, J = 8.1, 1.2 Hz, 1H), 6.81 (s, 1H), 2.45 – 2.38 (m, 2H), 2.30 (s, 3H), 1.58 – 1.49 (m, 2H), 1.36 – 1.18 (m, 19H), 0.87 (t, J = 6.9 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 191.1, 135.9, 134.5, 129.2 (two signals overlapped), 128.7, 126.7, 40.5, 33.5, 32.1, 32.7, 30.0, 29.7, 29.5, 29.0, 22.9, 21.2, 14.3; HRMS (ESI) Calcd for C20H34N [M + H]+ 288.2691, found 288.2690.

2,2-dimethyl-1-(2-octyl-5-(trifluoromethyl)phenyl)propan-1-imine (3ja): Light yellow oil (53 mg, 77%); Rf 0.60 (hexane/EtOAc/NEt3 = 10/1/1); 1H NMR (400 MHz, CDCl3): δ 9.22 (brs, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.27 – 7.26 (m, 1H), 2.55 – 2.48 (m, 2H), 1.63 – 1.53 (m, 2H), 1.39 – 1.19 (m, 19H), 0.91 – 0.83 (m, 3H); 13C NMR (100 MHz, CDCl3): δ 189.3, 143.5, 141.8, 129.9, 127.6 (q, 2J_C-F = 32.7 Hz), 124.75 (q, 3J_C-F = 3.5 Hz), 124.3 (d, 1J_C-F = 274.0 Hz), 123.19 (d, 3J_C-F = 5.8 Hz), 40.7, 33.9, 32.1, 31.7, 30.0, 29.6, 29.4, 28.8, 22.9, 14.3; HRMS (ESI) Calcd for C20H31NF3 [M + H]+ 342.2409, found 342.2407.

2,2-Dimethyl-1-(5-methyl-2-octylphenyl)propan-1-imine (3ka): Silica gel chromatography (eluent: hexane/EtOAc/NEt3 = 50/1/1) of the crude product afforded a mixture of the title compound and its regioisomer 3ka’ as a light yellow oil (52 mg, 85%). The ratio of 3ka and 3ka’ was determined to be 4:1 by 1H NMR analysis.

Rf 0.50 (hexane/EtOAc/NEt3 = 10/1/1); 1H NMR (3ka, 400 MHz, CDCl3): δ 7.15 (d, J = 8.6 Hz, 1H), 6.80 (dd, J = 8.6, 2.7 Hz, 1H), 6.54 (d, J = 2.7 Hz, 1H), 3.77 (s, 3H), 2.42 – 2.35 (m, 2H), 1.58 – 1.47 (m, 2H), 1.34 – 1.19 (m, 19H), 0.87 (t, J = 6.8 Hz, 3H); 13C NMR (3ka, 100 MHz, CDCl3): δ 190.7, 156.8, 142.4, 131.1, 130.4, 113.4, 111.9, 55.5, 40.5, 33.1, 32.2, 32.1, 30.0, 29.7, 29.0, 22.9, 14.3; HRMS (ESI) Calcd for C20H34NO [M + H]+ 304.2640, found 304.2645.
2,2-Dimethyl-1-(4-octylbenzo[d][1,3]dioxol-5-yl)propan-1-imine (3la): Silica gel chromatography (eluent: hexane/EtOAc/NEt$_3$ = 50/1/1) of the crude product afforded a mixture of the title compound and its regioisomer 3la' as a light yellow oil (52 mg, 82%). The ratio of 3la and 3la' was determined to be 3:2 by $^1$H NMR analysis.

$R_f$ 0.50 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.16 (s, 1H for each isomer), 6.70 (s, 1H for 3la'), 6.62 (d, $J$ = 8.0 Hz, 1H for 3la), 6.50 (d, $J$ = 8.1 Hz, 1H for each isomer), 5.94 (s, 2H for 3la), 5.92 (s, 2H for 3la'), 2.44 – 2.32 (m, 2H for each isomer), 1.56 – 1.47 (m, 2H for each isomer), 1.37 – 1.17 (m, 19H for each isomer), 0.86 (t, $J$ = 6.6 Hz, 3H for each isomer); $^{13}$C NMR (both isomers, 100 MHz, CDCl$_3$): $\delta$ 190.4, 190.0, 147.3, 146.5, 146.3, 144.9, 136.0, 132.9, 121.8, 119.4, 109.2, 106.5, 105.6, 101.2, 101.0, 40.6, 33.8, 32.2, 32.1, 30.6, 30.2, 29.9, 29.7, 29.6, 29.4, 29.1, 29.0, 22.9, 14.3; HRMS (ESI) Calcd for C$_{20}$H$_{32}$NO$_2$ [M + H]$^+$ 318.2433, found 318.2435.

2,2-Dimethyl-1-(3-octynaphthalen-2-yl)propan-1-imine (3ma): Light yellow oil (55 mg, 85%); $R_f$ 0.58 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.89 (brs, 1H), 7.78 (dd, $J$ = 7.5, 1.9 Hz, 2H), 7.71 (s, 1H), 7.49 (s, 1H), 7.48 – 7.41 (m, 2H), 2.67 – 2.60 (m, 2H), 1.74 – 1.62 (m, 2H), 1.46 – 1.21 (m, 19H), 0.89 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.9, 140.5, 137.3, 133.1, 131.2, 127.9, 127.6, 127.4, 126.4, 125.9, 124.8, 40.8, 34.0, 32.1, 31.8, 30.0, 29.7, 29.5, 29.0, 22.9, 14.3; HRMS (ESI) Calcd for C$_{23}$H$_{34}$N [M + H]$^+$ 324.2691, found 324.2686.
1-(3,5-Difluoro-2-octylphenyl)-2,2-dimethylpropan-1-imine (3na): Light yellow oil (48 mg, 78%); \( R_f \) 0.58 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.23 (brs, 1H), 6.76 – 6.71 (m, 1H), 6.58 (d, \( J = 8.4 \) Hz, 1H), 2.48 – 2.33 (s, 2H), 1.54 – 1.42 (m, 2H), 1.36 – 1.17 (m, 19H), 0.87 (t, \( J = 6.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 188.4, 161.9 (dd, \(^1\)J\(_{C-F}\) = 248.8 Hz, \(^3\)J\(_{C-F}\) = 12.2 Hz), 160.4 (dd, \(^1\)J\(_{C-F}\) = 247.3 Hz, \(^2\)J\(_{C-F}\) = 12.8 Hz), 144.0, 122.9, 109.2 (d, \(^2\)J\(_{C-F}\) = 23.0 Hz), 103.3 (t, \(^2\)J\(_{C-F}\) = 25.9 Hz), 40.6, 32.1, 30.9, 30.2, 29.5, 29.4, 28.9, 28.1, 22.9, 14.3; HRMS (ESI) Calcd for C\(_{19}\)H\(_{30}\)NF\(_2\) [M + H]\(^+\) 310.2346, found 310.2343.

![NMR spectrum of 3na](image)

1-(2-Cyclohexyl-4-methylphenyl)-2,2-dimethylpropan-1-imine (3bn): Light yellow oil (43 mg, 83%); \( R_f \) 0.57 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.09 (brs, 1H), 7.10 (s, 1H), 6.94 (d, \( J = 7.7 \) Hz, 1H), 6.88 (d, \( J = 7.8 \) Hz, 1H), 2.38 – 2.28 (m, 4H), 1.83 – 1.66 (m, 4H), 1.56 – 1.17 (m, 15H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 191.2, 144.0, 138.4, 137.6, 127.6, 126.1, 125.9, 42.2, 40.6, 29.0, 27.1 (two signals overlapped), 26.3, 21.6; HRMS (ESI) Calcd for C\(_{18}\)H\(_{28}\)N [M + H]\(^+\) 258.2222, found 258.2224.

![NMR spectrum of 3bn](image)

1-(2-Cyclohexyl-4-(methylthio)phenyl)-2,2-dimethylpropan-1-imine (3fn): Light yellow oil (39 mg, 68%); \( R_f \) 0.53 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.16 (brs, 1H), 7.18 (d, \( J = 1.9 \) Hz, 1H), 7.01 (dd, \( J = 8.1, 1.9 \) Hz, 1H), 6.92 (d, \( J = 8.1 \) Hz, 1H), 2.49 (s, 3H), 2.38 – 2.30 (m, 1H), 1.83 – 1.63 (m, 4H), 1.46 – 1.24 (m, 6H), 1.22 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 190.6, 144.8, 138.1 (two signals overlapped), 126.8, 125.3, 123.2, 42.3, 40.7, 28.9, 27.0 (two signals overlapped), 26.3, 16.0; HRMS (ESI) Calcd for C\(_{18}\)H\(_{28}\)NS [M + H]\(^+\) 290.1942, found 290.1938.
1-(2-Cyclohexyl-5-methylphenyl)-2,2-dimethylpropan-1-imine (3in): Light yellow oil (37 mg, 71%); $R_f$ 0.61 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.10 (brs, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.09 (dd, $J = 7.8$, 1.6 Hz, 1H), 6.79 (d, $J = 1.0$ Hz, 1H), 2.37 – 2.27 (m, 4H), 1.79 – 1.70 (m, 4H), 1.51 – 1.19 (m, 15H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.2, 141.1, 134.6, 128.9 (two signals overlapped), 126.8, 126.6, 41.9, 40.5, 29.0, 27.2 (two signals overlapped), 26.35, 21.21; HRMS (ESI) Calcd for C$_{18}$H$_{28}$N [M + H]$^+$ 258.2222, found 258.2224.

1-(3-Cyclohexynaphthalen-2-yl)-2,2-dimethylpropan-1-imine (3mn): Light yellow oil (48 mg, 81%); $R_f$ 0.58 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.24 (brs, 1H), 7.78 (t, $J = 7.0$ Hz, 2H), 7.75 (s, 1H), 7.49 – 7.40 (m, 3H), 2.46 (t, $J = 11.5$ Hz, 1H), 1.95 – 1.73 (m, 6H), 1.46 – 1.24 (m, 13H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.0, 142.6, 140.3, 133.1, 131.1, 127.7, 127.4, 126.2, 125.8, 125.4, 124.6, 42.3, 40.7, 28.9, 27.2 (two signals overlapped), 26.2; HRMS (ESI) Calcd for C$_{21}$H$_{28}$N [M + H]$^+$ 294.2222, found 294.2224.
**Cobalt-Catalyzed ortho-Arylation of Pivalophenone N–H Imines with Aryl Chlorides**

**Table S2. Screening of Reaction Conditions**

![Chemical Structures]

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<td>Co(acac)₃</td>
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ᵃ Determined by GC using n-tridecane as an internal standard. ᵇ 2.5 equiv of t-BuCH₂MgBr was used. ᶜ TMEDA (80 mol%) was added. ᵈ Isolated yield.
General Procedure: 1-(4’-Methoxy-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5aa).

In a Schlenk tube were placed L2•HBr (7.5 mg, 0.020 mmol), Co(acac)3 (6.8 mg, 0.020 mmol), and THF (0.3 mL). The resulting solution was cooled in an ice bath, followed by the addition of t-BuCH2MgBr (2.0 M in THF, 0.25 mL, 0.50 mmol). After stirring for 30 min, TMEDA (24 µL, 0.16 mmol), 2,2-dimethyl-1-phenylpropan-1-imine (1a, 33 mg, 0.20 mmol), and 1-bromo-4-methoxybenzene (4a, 37 µL, 0.30 mmol) were added sequentially. The resulting mixture was warmed to room temperature and stirred for 12 h, and then filtered through a short pad of silica gel, which was washed with ethyl acetate (5 mL). The filtrate was concentrated under reduced pressure. Silica gel chromatography (eluent: hexane/EtOAc/NEt3 = 30/1/1) of the crude product afforded the title compound as a colorless oil (45 mg, 84%).

Rf 0.24 (hexane/EtOAc/NEt3 = 10/1/1); 1H NMR (400 MHz, CDCl3): δ 9.63 (brs, 1H), 7.44 – 7.25 (m, 5H), 7.16 – 7.08 (m, 1H), 6.96 – 6.86 (m, 2H), 3.82 (s, 3H), 0.89 (s, 9H); 13C NMR (100 MHz, CDCl3): δ 191.8, 159.1, 141.2, 138.2, 134.2, 131.2, 130.2, 128.2, 127.8, 126.6, 113.7, 55.4, 40.6, 28.8; HRMS (ESI) Calcd for C18H22NO [M + H]+ 268.1701, found 268.1704.

2,2-Dimethyl-1-(4'-methyl-[1,1'-biphenyl]-2-yl)propan-1-imine (5ac): Light yellow oil (42 mg, 83%); Rf 0.46 (hexane/EtOAc/NEt3 = 10/1/1); 1H NMR (400 MHz, CDCl3): δ 9.27 (brs, 1H), 7.41 – 7.24 (m, 5H), 7.16 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.4 Hz, 1H), 2.37 (s, 3H), 0.89 (s, 9H); 13C NMR (100 MHz, CDCl3): δ 191.7, 141.2, 138.8, 138.6, 137.2, 130.4, 130.0, 129.1, 128.2, 127.8, 126.8, 40.6, 28.9, 21.4; HRMS (ESI) Calcd for C18H22N [M + H]+ 252.1752, found 252.1754.
1-(4'-Fluoro-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ad): Light yellow oil (40 mg, 79%); Rf 0.41 (hexane/EtOAc/NEt₃ = 10/1/1); ¹H NMR (400 MHz, CDCl₃): δ 9.61 (br s, 1H), 7.41 – 7.30 (m, 5H), 7.13 (d, J = 7.7 Hz, 1H), 7.08 – 7.01 (m, 2H), 0.88 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 191.4, 162.4 (d, ¹J_C-F = 246.9 Hz), 141.2, 137.7 (d, ⁴J_C-F = 3.3 Hz), 137.6, 131.8 (d, ³J_C-F = 7.9 Hz), 130.3, 128.3, 128.0, 127.1, 115.3 (d, ²J_C-F = 21.4 Hz), 40.7, 28.8; HRMS (ESI) Calcd for C₁₇H₁₉NF [M + H]⁺ 256.1502, found 256.1507.

2,2-Dimethyl-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)propan-1-imine (5ae): Light yellow oil (42 mg, 68%); Rf 0.40 (hexane/EtOAc/NEt₃ = 10/1/1); ¹H NMR (400 MHz, CDCl₃): δ 9.69 (br s, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 7.9 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.20 – 7.16 (m, 1H), 0.88 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 190.8, 145.4, 141.0, 137.3, 130.6, 130.31, 129.7 (q, ²J_C-F = 32.5 Hz), 128.5, 128.1, 127.8, 125.3 (q, ³J_C-F = 3.4 Hz), 124.4 (q, ¹J_C-F = 272.0 Hz), 40.8, 28.8; HRMS (ESI) Calcd for C₁₈H₁₉NF₃ [M + H]⁺ 306.1470, found 306.1472.

2'-(1-Imino-2,2-dimethylpropyl)-N,N-dimethyl-[1,1'-biphenyl]-4-amine (5af): Light yellow oil (45 mg, 81%); Rf 0.35 (hexane/EtOAc/NEt₃ = 10/1/1); ¹H NMR (400 MHz, CDCl₃): δ 9.28 (brs, 1H), 7.39 – 7.31 (m, 2H), 7.28 – 7.23 (m, 3H), 7.09 (d, J = 7.4 Hz, 1H), 6.74 – 6.69 (m, 2H), 2.97 (s, 6H), 0.91 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 192.4, 149.9, 141.2, 138.8, 130.8, 130.2, 129.8, 128.2, 127.9, 126.0, 112.3, 40.7, 40.6, 29.0; HRMS (ESI) Calcd for C₁₉H₂₅N₂ [M +
1-(4′-((tert-Butyldimethylsilyl)oxy)-[1,1′-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ag): Light yellow oil (57 mg, 78%); \( R_f \) 0.34 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.25 (brs, 1H), 7.39 – 7.27 (m, 3H), 7.23 (d, \( J = 8.5 \) Hz, 2H), 7.11 – 7.08 (m, 1H), 6.85 – 6.81 (m, 2H), 0.99 (s, 9H), 0.87 (s, 9H), 0.20 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 192.0, 155.4, 138.3, 134.9, 131.3, 130.2, 128.2, 127.9, 126.9, 126.6, 120.1, 40.6, 28.9, 28.1, 26.0, -4.2; HRMS (ESI) Calcd for C\(_{23}\)H\(_{34}\)NOSi [M + H]\(^+\) 368.2410, found 368.2409.

2,2-Dimethyl-1-(4′-(trimethylsilyl)-[1,1′-biphenyl]-2-yl)propan-1-imine (5ah): Light yellow oil (50 mg, 81%); \( R_f \) 0.46 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.57 (brs, 1H), 7.53 – 7.48 (m, 2H), 7.43 – 7.29 (m, 1H), 7.14 (d, \( J = 7.3 \) Hz, 5H), 0.88 (s, 9H), 0.28 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 191.5, 142.0, 141.3, 139.5, 138.6, 133.3, 130.4, 129.5, 128.2, 127.8, 127.0, 40.6, 28.9, -0.9; HRMS (ESI) Calcd for C\(_{20}\)H\(_{28}\)NSi [M + H]\(^+\) 310.1991, found 310.1997.

2,2-Dimethyl-1-(3′-methyl-[1,1′-biphenyl]-2-yl)propan-1-imine (5ai): Light yellow oil (41 mg, 82%); \( R_f \) 0.45 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.57 (brs, 1H), 7.40 – 7.29 (m, 3H), 7.26 – 7.21 (m, 1H), 7.20 – 7.14 (m, 2H), 7.12 (d, \( J = 7.4 \) Hz, 2H), 2.36 (s,
3H), 0.88 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.7, 141.6, 141.3, 138.6, 137.9, 130.9, 130.3, 128.2, 128.2, 127.8, 127.3, 126.9, 40.6, 29.0, 21.7; HRMS (ESI) Calcd for C\(_{18}\)H\(_{22}\)N [M + H]\(^+\) 252.1752, found 252.1756.

1-(3'-Fluoro-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5aj): Light yellow oil (38 mg, 75%); \(R_f\) 0.45 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.65 (brs, 1H), 7.43 – 7.29 (m, 4H), 7.05 – 6.98 (m, 1H), 0.90 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.0, 162.6 (d, \(^1\)J\(_{C-F}\) = 246.1 Hz), 143.7 (d, \(^4\)J\(_{C-F}\) = 8.1 Hz), 137.2, 130.1, 129.7 (d, \(^3\)J\(_{C-F}\) = 8.3 Hz), 128.2, 128.0 (d, \(^3\)J\(_{C-F}\) = 8.5 Hz), 127.3, 126.7, 125.9 (d, \(^4\)J\(_{C-F}\) = 2.4 Hz), 117.0 (d, \(^2\)J\(_{C-F}\) = 21.8 Hz), 114.2 (d, \(^2\)J\(_{C-F}\) = 21.0 Hz), 40.6, 28.7; HRMS (ESI) Calcd for C\(_{17}\)H\(_{19}\)NF [M + H]\(^+\) 256.1502, found 256.1498.

1-(3'-Methoxy-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ak): Light yellow oil (45 mg, 84%); \(R_f\) 0.30 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.58 (brs, 1H), 7.41 – 7.30 (m, 3H), 7.27 (t, \(J\) = 7.9 Hz, 1H), 7.13 (d, \(J\) = 7.4 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.88 – 6.84 (m, 1H), 3.80 (s, 3H), 0.90 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.7, 159.5, 143.1, 141.2, 138.4, 130.2, 129.4, 128.2, 128.0, 127.1, 122.7, 115.6, 113.3, 55.5, 40.7, 28.9; HRMS (ESI) Calcd for C\(_{18}\)H\(_{22}\)NO [M + H]\(^+\) 268.1701, found 268.1702.
2,2-Dimethyl-1-(3'-trifluoromethyl)-[1,1'-biphenyl]-2-yl)propan-1-imine (5al): Light yellow oil (37 mg, 61%); $R_f$ 0.45 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.69 (brs, 1H), 7.67 (s, 1H), 7.58 (d, $J$ = 7.7 Hz, 2H), 7.51 – 7.34 (m, 4H), 7.18 (d, $J$ = 7.4 Hz, 1H), 0.87 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.9, 142.4, 137.2, 133.6, 130.8 (q, $^2J_{C-F}$ = 32.2 Hz), 130.6, 130.3, 128.8, 128.5, 128.1, 127.7, 127.0 (q, $^3J_{C-F}$ = 3.2 Hz), 124.3 (q, $^1J_{C-F}$ = 272.4 Hz), 124.2 (q, $^3J_{C-F}$ = 3.6 Hz), 40.8, 28.8; HRMS (ESI) Calcd for C$_{18}$H$_{19}$NF$_3$ [M + H]$^+$ 306.1470, found 306.1471.

![Chemical structure](image)

2,2-Dimethyl-1-(2'-methyl-[1,1'-biphenyl]-2-yl)propan-1-imine (5am): Light yellow oil (34 mg, 67%); $R_f$ 0.45 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.14 (brs, 1H), 7.38 – 7.30 (m, 2H), 7.25 – 7.21 (m, 3H), 7.18 – 7.14 (m, 3H), 2.21 (s, 3H), 0.91 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.0, 142.1, 140.4, 137.7, 136.1, 131.4, 131.1, 130.5, 127.8, 127.6, 127.5, 126.9, 125.3, 40.3, 29.1, 20.8; HRMS (ESI) Calcd for C$_{18}$H$_{21}$N [M + H]$^+$ 252.1752, found 252.1749.

![Chemical structure](image)

1-(2'-Fluoro-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5an): Light yellow oil (33 mg, 65%); $R_f$ 0.46 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.54 (brs, 1H), 7.41 – 7.24 (m, 5H), 7.20 – 7.16 (m, 1H), 7.15 – 7.07 (m, 2H), 0.93 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.2, 159.8 (d, $^1J_{C-F}$ = 246.0 Hz), 142.0, 132.9, 132.4, 131.2, 129.8 (d, $^3J_{C-F}$ = 8.0 Hz), 128.9 (d, $^2J_{C-F}$ = 15.6 Hz), 127.8, 127.6, 127.4, 123.8 (d, $^3J_{C-F}$ = 3.3 Hz), 115.9 (d, $^2J_{C-F}$ = 22.8 Hz), 40.4, 28.9; HRMS (ESI) Calcd for C$_{17}$H$_{19}$NF [M + H]$^+$ 256.1502, found 256.1500.
1-(2'-Methoxy-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ao): Light yellow oil (38 mg, 71%); $R_f$ 0.35 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.29 (brs, 1H), 7.38 – 7.26 (m, 4H), 7.15 – 7.13 (m, 2H), 6.96 – 6.93 (m, 1H), 6.90 (d, $J$ = 8.3 Hz, 1H), 3.75 (s, 3H), 0.94 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.4, 156.7, 135.4, 132.2, 131.2, 130.3, 129.3, 127.6, 126.9 (two signals overlapped), 126.7, 120.2, 110.8, 55.4, 40.0, 29.2; HRMS (ESI) Calcd for C$_{18}$H$_{22}$NO [M + H]$^+$ 268.1701, found 268.1700.

2,2-Dimethyl-1-(2'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)propan-1-imine (5ap): Light yellow oil (28 mg, 45%); $R_f$ 0.45 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.42 (brs, 1H), 7.74 – 7.71 (m, 1H), 7.52 – 7.42 (m, 2H), 7.38 – 7.29 (m, 4H), 7.24 – 7.20 (m, 1H), 1.02 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 189.8, 141.5, 139.4, 135.8, 132.9, 131.1, 131.0, 129.2 (q, $^2$J$_{C-F}$ = 29.4 Hz), 128.0, 127.5, 127.3, 127.2, 127.0 (q, $^3$J$_{C-F}$ = 5.2 Hz), 124.4 (q, $^1$J$_{C-F}$ = 274.1 Hz), 40.2, 29.4; HRMS (ESI) Calcd for C$_{18}$H$_{19}$NF$_3$ [M + H]$^+$ 306.1470, found 306.1469.

1-(2-(Benzo[dd][1,3]dioxol-5-yl)phenyl)-2,2-dimethylpropan-1-imine (5aq): Light yellow oil (47 mg, 84%); $R_f$ 0.33 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.58 (brs, 1H), 7.39 – 7.27 (m, 3H), 7.13 – 7.08 (m, 1H), 6.89 – 6.78 (m, 3H), 5.98 (s, 2H), 0.92 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.7, 147.7, 147.1, 141.2, 138.2, 135.7, 130.3, 128.3, 128.0,
126.8, 123.9, 110.6, 108.2, 101.3, 40.7, 29.0; HRMS (ESI) Calcd for C_{18}H_{20}NO_2 [M + H]^+ 282.1494, found 282.1499.

1-(2',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ar): Light yellow oil (47 mg, 79%); R_f 0.31 (hexane/EtOAc/NEt_3 = 10/1/1); ^1H NMR (400 MHz, CDCl_3): δ 9.40 (brs, 1H), 7.38 – 7.25 (m, 3H), 7.14 (dd, J = 7.1, 1.2 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.74 (d, J = 2.6 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 0.96 (s, 9H); ^13C NMR (100 MHz, CDCl_3): δ 190.2, 153.1, 151.0, 135.7, 131.1, 131.0, 127.6, 127.0, 126.8, 118.1, 114.1, 111.7 (two signals overlapped), 56.1, 55.8, 40.0, 29.2; HRMS (ESI) Calcd for C_{19}H_{24}NO_2 [M + H]^+ 298.1807, found 298.1805.

2,2-Dimethyl-1-(2-(naphthalen-2-yl)phenyl)propan-1-imine (5as): Light yellow oil (41 mg, 72%); R_f 0.41 (hexane/EtOAc/NEt_3 = 10/1/1); ^1H NMR (400 MHz, CDCl_3): δ 9.71 (brs, 1H), 7.88 – 7.81 (m, 4H), 7.57 – 7.41 (m, 5H), 7.37 (td, J = 7.3, 1.9 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 0.86 (s, 9H); ^13C NMR (100 MHz, CDCl_3): δ 191.6, 141.4, 139.2, 138.3, 133.3, 132.6, 130.7, 129.2, 128.4, 128.3 (two signals overlapped), 128.0, 128.0, 127.8, 127.1, 126.5, 126.4, 40.7, 29.0; HRMS (ESI) Calcd for C_{21}H_{22}N [M + H]^+ 288.1752, found 288.1755.

2,2-Dimethyl-1-(2-(naphthalen-1-yl)phenyl)propan-1-imine (5at): Light yellow oil (29 mg,
52%); \( R_f \) 0.41 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.44 (s, 1H), 7.87 (d, \( J = 8.4 \) Hz, 1H), 7.83 (d, \( J = 8.3 \) Hz, 1H), 7.71 (d, \( J = 8.1 \) Hz, 1H), 7.49 – 7.34 (m, 7H), 7.28 – 7.24 (m, 1H), 0.82 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 190.6, 142.7, 138.4, 136.6, 133.9, 132.6, 132.0, 129.0, 128.6, 128.2, 127.7, 127.4, 127.2, 126.4, 126.3, 125.9, 125.0, 40.3, 29.2; HRMS (ESI) Calcd for C\(_{21}\)H\(_{22}\)N [M + H]\(^+\) 288.1752, found 288.1748.

![Chemical Structure](image)

**1-(4'-Methoxy-5-methyl-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ba):** Light yellow oil (45 mg, 80%); \( R_f \) 0.36 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.50 (brs, 1H), 7.28 (d, \( J = 8.4 \) Hz, 2H), 7.14 (s, 1H), 7.12 – 7.08 (m, 1H), 7.00 (d, \( J = 7.7 \) Hz, 1H), 6.91 – 6.86 (m, 2H), 3.82 (s, 3H), 2.39 (s, 3H), 0.89 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 192.0, 159.1, 138.1, 137.9 (two signals overlapped), 134.4, 131.2, 131.0, 127.8, 127.2, 113.7, 55.5, 40.6, 28.9, 21.4; HRMS (ESI) Calcd for C\(_{19}\)H\(_{24}\)NO [M + H]\(^+\) 282.1858, found 282.1859.

![Chemical Structure](image)

**1-(4''-Methoxy-[1,1':3',1''-terphenyl]-4'-yl)-2,2-dimethylpropan-1-imine (5ca):** Light yellow oil (53 mg, 78%); \( R_f \) 0.35 (hexane/EtOAc/NEt\(_3\) = 10/1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.57 (brs, 1H), 7.65 – 7.61 (m, 2H), 7.56 (d, \( J = 1.8 \) Hz, 1H), 7.53 (dd, \( J = 7.8, 1.8 \) Hz, 1H), 7.45 (t, \( J = 7.6 \) Hz, 2H), 7.39 – 7.32 (m, 3H), 7.19 (d, \( J = 7.9 \) Hz, 1H), 6.94 – 6.90 (m, 2H), 3.84 (s, 3H), 0.93 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 191.8, 159.2, 141.1, 140.6, 140.1, 138.8, 134.2, 131.3, 129.1 (two signals overlapped), 128.5, 127.8, 127.3, 125.2, 113.9, 55.5, 40.8, 28.9; HRMS (ESI) Calcd for C\(_{24}\)H\(_{26}\)NO [M + H]\(^+\) 344.2014, found 344.2019.
1-(4',5-Dimethoxy-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5da): Light yellow oil (48 mg, 81%); $R_f$ 0.25 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.50 (brs, 1H), 7.29 (d, $J = 8.5$ Hz, 2H), 7.03 (d, $J = 8.1$ Hz, 1H), 6.92 – 6.81 (m, 4H), 3.83 (s, 3H), 3.82 (s, 3H), 0.88 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.8, 159.2, 139.8, 134.2, 134.0, 131.1, 129.1 (two signals overlapped), 115.5, 113.8, 112.1, 55.5, 55.5, 40.7, 28.9; HRMS (ESI) Calcd for C$_{19}$H$_{24}$NO$_2$ [M + H]$^+$ 298.1807, found 298.1805.

1-(4'-Methoxy-5-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ea): Light yellow oil (55 mg, 78%); $R_f$ 0.27 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.68 (brs, 1H), 7.30 (d, $J = 7.5$ Hz, 2H), 7.18 (s, 1H), 7.14 (s, 2H), 6.90 (dd, $J = 8.5$, 1.6 Hz, 2H), 3.83 (s, 3H), 0.87 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.8, 159.6, 148.9, 140.0 (d, $^2J_{C-F}$ = 257.6 Hz), 118.8, 114.0, 55.5, 40.8, 28.8; HRMS (ESI) Calcd for C$_{19}$H$_{21}$NO$_2$F$_3$ [M + H]$^+$ 352.1524, found 352.1530.

1-(5-Fluoro-4'-methoxy-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ha): Light yellow oil (45 mg, 79%); $R_f$ 0.35 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.62 (brs, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.10 – 6.96 (m, 3H), 6.92 – 6.87 (m, 2H), 3.82 (s, 3H), 0.87 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.1, 162.3 (d, $^1J_{C-F}$ = 247.1 Hz), 159.5, 140.6, 137.2, 133.1, 131.1, 129.6 (d, $^3J_{C-F}$ = 8.1 Hz), 116.9 (d, $^2J_{C-F}$ = 21.3 Hz), 113.9, 113.4 (d, $^2J_{C-F}$ =
21.1 Hz), 55.5, 40.8, 28.8; HRMS (ESI) Calcd for C_{18}H_{21}NOF [M + H]^+ 286.1607, found 286.1613.

1-(4′-Methoxy-4-methyl-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-imine (5ia): Light yellow oil (41 mg, 73%); R_f 0.37 (hexane/EtOAc/NEt_3 = 10/1/1); ^1H NMR (400 MHz, CDCl_3): δ 9.57 (brs, 1H), 7.30 – 7.25 (m, 2H), 7.22 – 7.16 (m, 2H), 6.91 – 6.86 (m, 3H), 3.82 (s, 3H), 2.38 (s, 3H), 0.88 (s, 9H); ^13C NMR (100 MHz, CDCl_3): δ 192.1, 159.0, 141.1, 136.3, 135.4, 134.3, 131.2, 130.2, 129.0, 128.5, 113.8, 55.5, 40.6, 29.0, 21.3; HRMS (ESI) Calcd for C_{19}H_{22}NO [M + H]^+ 282.1858, found 282.1861.

1-(4-(4-Methoxyphenyl)benzo[d][1,3]dioxol-5-yl)-2,2-dimethylpropan-1-imine (5la): Light yellow oil (51 mg, 82%); R_f 0.31 (hexane/EtOAc/NEt_3 = 10/1/1); ^1H NMR (400 MHz, CDCl_3): δ 9.52 (brs, 1H), 7.33 (d, J = 8.7 Hz, 2H), 6.94 – 6.88 (m, 2H), 6.76 (d, J = 8.0 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 5.96 (s, 2H), 3.82 (s, 3H), 0.89 (s, 9H); ^13C NMR (100 MHz, CDCl_3): δ 191.0, 159.4, 147.0, 145.3, 136.0, 131.9, 127.3, 121.2, 120.8, 113.9, 107.0, 101.2, 55.5, 40.6, 29.0; HRMS (ESI) Calcd for C_{19}H_{22}NO_3 [M + H]^+ 312.1600, found 312.1596.
1-(3-(4-Methoxyphenyl)naphthalen-2-yl)-2,2-dimethylpropan-1-imine (5na): Silica gel chromatography (eluent: hexane/EtOAc/NEt$_3$ = 30/1/1) of the crude product afforded a mixture of the title compound and its regioisomer 5na' as a light yellow oil (48 mg, 75%). The ratio of 5na and 5na' was determined to be 3:2 by $^1$H NMR analysis.

$R_f$ 0.35 (hexane/EtOAc/NEt$_3$ = 10/1/1); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.62 (s, 1H for each isomer), 7.90 – 7.80 (m, 4H for each isomer), 7.79 (s, 1H for 5na), 7.65 (d, $J = 8.5$ Hz, 1H for 5na'), 7.59 (s, 1H for 5na), 7.54 – 7.46 (m, 4H for each isomer), 7.43 – 7.37 (m, 3H for each isomer), 7.29 – 7.24 (m, 2H for each isomer), 7.00 – 6.92 (m, 4H for each isomer), 3.87 (s, 3H for 5na'), 3.85 (s, 3H for 5na), 0.97 (s, 9H for 5na'), 0.95 – 0.89 (m, 9H for 5na); $^{13}$C NMR (both isomers, 100 MHz, CDCl$_3$): δ 192.1, 191.3, 159.2, 159.2, 140.2, 139.8, 136.7, 135.1, 134.2, 133.16, 133.15, 133.13, 133.11, 131.8, 131.6, 130.5, 129.0, 128.1, 127.9, 127.2, 127.1, 126.8, 126.7, 126.6, 126.4, 126.2, 124.8, 113.9, 113.5, 55.53, 55.51, 40.7, 40.2, 29.4, 29.0; HRMS (ESI) Calcd for C$_{22}$H$_{24}$NO [M + H]$^+$ 318.1858, found 318.1860.
Synthesis of ortho-Substituted Benzonitriles

Conditions A: 3aa or 5aa (0.20 mmol) was weighed in a 4 mL vial containing a stir bar, and then dissolved in t-BuOOt-Bu (0.5 mL). The vial was placed in Luzchem LZF-4V photoreactor and irradiated at 254 nm for 12 h. The mixture was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography (eluent: hexane/EtOAc = 100/1 for ortho-alkylbenzonitrile, 30/1 for ortho-arylbenzonitrile) to afford the desired benzonitrile derivative.

Conditions B: In a 10 mL Schlenk tube containing a stir bar were placed 3aa or 5aa (0.20 mmol) and Cu(OAc)$_2$ (3.6 mg, 0.020 mmol), followed by the addition of DMF (2 mL). An oxygen balloon was attached to the Schlenk tube, and the reaction mixture was stirred at 80 °C for 12 h. The mixture was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography (eluent: hexane/EtOAc = 100/1 for ortho-alkylbenzonitrile, 30/1 for ortho-arylbenzonitrile) to afford the desired benzonitrile derivative.

2-Octylbenzonitrile (7a): Colorless oil; $R_f$ 0.65 (hexane/EtOAc = 1/10); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.60 (d, $J = 7.7$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 1H), 7.32 – 7.24 (m, 2H), 2.86 – 2.80 (m, 2H), 1.70 – 1.63 (m, 2H), 1.40 – 1.21 (m, 10H), 0.88 (t, $J = 6.7$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.1, 133.0, 132.9, 129.7, 126.5, 118.4, 112.6, 34.9, 32.1, 31.2, 29.6, 29.5, 29.4, 22.9, 14.3; HRMS (ESI) Calcd for C$_{15}$H$_{22}$N [M + H]$^+$ 216.1752, found 216.1760.

4'-Methoxy-[1,1'-biphenyl]-2-carbonitrile (7b): Colorless oil; $R_f$ 0.32 (hexane/EtOAc = 1/10); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.74 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.62 (td, $J = 7.8$, 1.3 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.40 (td, $J = 7.6$, 1.0 Hz, 1H), 7.04 – 7.00 (m, 2H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 160.3, 145.4, 134.0, 133.0, 130.8, 130.2, 130.1, 127.3, 119.2, 114.4, 111.3, 55.6; HRMS (ESI) Calcd for C$_{14}$H$_{12}$NO [M + H]$^+$ 210.0919, found 210.0915.
Two-Step Synthesis of ortho-Substituted Benzonitriles

**Procedure A:** 2-(Pent-4-en-1-yl)benzonitrile (7d). The reaction of 2,2-dimethyl-1-phenylpropan-1-imine (1a, 33 mg, 0.20 mmol) and 5-bromopent-1-ene (2g, 36 µL, 0.30 mmol) was performed according to the typical procedure described above. The reaction mixture was filtered through a short pad of silica gel, washing with ethyl acetate (5 mL). The filtrate was concentrated under reduced pressure. The residue was dissolved in a small amount (ca. 1 mL) of CH₂Cl₂, transferred to a 4 mL vial, and then concentrated again under reduced pressure. A stir bar was placed in this vial, and t-BuOOt-Bu (0.5 mL) was added. The vial was placed in Luzchem LZC-4V photoreactor and irradiated at 254 nm for 12 h. The mixture was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography (eluent: hexane/EtOAc = 100/1) to afford the title compound as a colorless oil (27 mg, 78%).

$\text{R}_{f} 0.62$ (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.60 (d, $J = 7.7$ Hz, 1H), 7.50 (td, $J = 7.7, 1.2$ Hz, 1H), 7.33 – 7.28 (m, 2H), 5.88 – 5.78 (m, 1H), 5.09 – 4.97 (m, 2H), 2.85 (t, $J = 14.3$ Hz, 2H), 2.14 (dd, $J = 14.3, 7.1$ Hz, 2H), 1.82 – 1.74 (m, 2H); $^{13}$C NMR (100 MHz, CDCl₃): $\delta$ 146.6, 138.1, 133.0, 132.9, 129.8, 126.6, 118.3, 115.5, 112.6, 34.2, 33.4, 30.2; HRMS (ESI) Calcd for C₁₂H₁₄N [M + H]$^+$ 172.1126, found 172.1124.

**Procedure B:** 2-(3-Phenylpropyl)benzonitrile (7c). The reaction of 2,2-dimethyl-1-phenylpropan-1-imine (1a, 33 mg, 0.20 mmol) and (3-bromopropyl)benzene (2c, 46 µL, 0.30 mmol) was performed according to the typical procedure described above. The reaction mixture was filtered through a short pad of silica gel, washing with ethyl acetate (5 mL). The filtrate was concentrated under reduced pressure. The residue was dissolved in DMF (1 mL) and then transferred into a 10 mL Schelenk tube containing a stir bar, followed by the addition of Cu(OAc)$_2$ (3.6 mg, 0.020 mmol) and DMF (1 mL). The reaction mixture was stirred under oxygen atmosphere (using a balloon) at 80 °C for 12 h. The mixture was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography (eluent: hexane/EtOAc = 100/1) to afford the title compound as a colorless oil (36 mg, 81%).
$R_f$ 0.60 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (d, $J = 7.7$ Hz, 1H), 7.53 – 7.47 (m, 1H), 7.33 – 7.27 (m, 4H), 7.21 (d, $J = 7.3$ Hz, 3H), 2.90 (t, $J = 7.6$ Hz, 2H), 2.72 (t, $J = 7.7$ Hz, 2H), 2.07 – 1.98 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.5, 141.8, 133.1, 133.0, 129.70, 128.6 (two signals overlapped), 126.7, 126.2, 118.3, 112.6, 35.7, 34.4, 32.6; HRMS (ESI) Calcd for C$_{16}$H$_{16}$N [M + H]$^+$ 222.1283, found 222.1288.

![Cyclobutylmethylbenzonitrile](image)

**2-(Cyclobutylmethyl)benzonitrile (7e):** Light yellow oil (28 mg, 82%, procedure A); $R_f$ 0.60 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (dd, $J = 8.0$, 1.4 Hz, 1H), 7.48 (td, $J = 7.7$, 1.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 2.93 (d, $J = 7.6$ Hz, 2H), 2.71 – 2.60 (m, 1H), 2.09 – 1.98 (m, 2H), 1.91 – 1.73 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.4, 133.0, 132.8, 129.7, 126.6, 118.6, 112.6, 41.3, 36.9, 28.3, 18.5; HRMS (ESI) Calcd for C$_{12}$H$_{14}$N [M + H]$^+$ 172.1126, found 172.1126.

![Cyclohexylmethylbenzonitrile](image)

**2-(Cyclohexylmethyl)benzonitrile (7f):** Light yellow oil (32 mg, 81%, procedure A); $R_f$ 0.61 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (dd, $J = 8.0$, 1.4 Hz, 1H), 7.49 (td, $J = 7.7$, 1.4 Hz, 1H), 7.29 – 7.25 (m, 2H), 2.72 (d, $J = 6.9$ Hz, 2H), 1.74 – 1.60 (m, 5H), 1.23 – 1.13 (m, 4H), 1.08 – 0.98 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.7, 132.9, 132.6, 130.6, 126.5, 118.7, 113.1, 42.6, 39.8, 33.2, 26.6, 26.4; HRMS (ESI) Calcd for C$_{14}$H$_{18}$N [M + H]$^+$ 200.1439, found 200.1436.

![Neopentylbenzonitrile](image)

**2-Neopentylbenzonitrile (7g):** Light yellow oil (29 mg, 85%, procedure A); $R_f$ 0.61 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (d, $J = 7.7$, 1.2 Hz, 1H), 7.49 (td, $J = 7.8$, 1.4 Hz, 1H), 7.32 – 7.26 (m, 2H), 2.78 (s, 2H), 0.98 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.9, 133.0, 132.1, 131.8, 126.7, 119.3, 114.2, 48.0, 33.4, 29.6; HRMS (ESI) Calcd
for C_{12}H_{16}N [M + H]^+ 174.1283, found 174.1286.

2-Cyclohexylbenzonitrile (7h): \(^{10}\) Light yellow oil (30 mg, 82%, procedure A); \(R_f\) 0.57 (hexane/EtOAc = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.60 (dd, \(J = 7.7, 1.5\) Hz, 1H), 7.55 – 7.50 (m, 1H), 7.36 (dd, \(J = 8.0, 0.5\) Hz, 1H), 7.28 – 7.24 (m, 1H), 3.03 – 2.92 (m, 1H), 1.93 – 1.84 (m, 4H), 1.83 – 1.73 (m, 2H), 1.51 – 1.41 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 151.8, 133.2, 133.1, 126.8, 126.5, 118.5, 112.1, 43.0, 33.9, 26.8, 26.2; HRMS (ESI) Calcd for C\(_{13}\)H\(_{16}\)N [M + H]^+ 186.1283, found 186.1283.

4-Methyl-2-octylnitrene (7i): Light yellow oil (35 mg, 77%, procedure B); \(R_f\) 0.62 (hexane/EtOAc = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.48 (d, \(J = 7.9\) Hz, 1H), 7.11 (s, 1H), 7.07 (d, \(J = 8.1\) Hz, 1H), 2.81 – 2.74 (m, 2H), 2.38 (s, 3H), 1.69 – 1.60 (m, 2H), 1.40 – 1.20 (m, 10H), 0.88 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 147.0, 143.7, 132.9, 130.4, 127.4, 118.8, 109.5, 34.8, 32.1, 31.2, 29.6, 29.5, 29.4, 22.9, 22.0, 14.3; HRMS (ESI) Calcd for C\(_{16}\)H\(_{24}\)N [M + H]^+ 230.1911, found 230.1909.

3-Octyl-[1,1'-biphenyl]-4-carbonitrile (7j): Light yellow oil (46 mg, 79%, procedure A); \(R_f\) 0.55 (hexane/EtOAc = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.67 (d, \(J = 8.0\) Hz, 1H), 7.60 – 7.57 (m, 2H), 7.52 – 7.49 (m, 2H), 7.48 – 7.45 (m, 2H), 7.44 – 7.41 (m, 1H), 2.92 – 2.86 (m, 2H), 1.76 – 1.67 (m, 2H), 1.44 – 1.24 (m, 10H), 0.90 – 0.86 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 147.6, 145.8, 139.8, 133.4, 129.3, 128.7, 128.4, 127.5, 125.3, 118.6, 111.2, 35.0, 32.1, 31.3, 29.6 (two signals overlapped), 29.4, 22.9, 14.3; HRMS (ESI) Calcd for C\(_{21}\)H\(_{28}\)N [M + H]^+ 292.2065,
found 292.2070.

![Chemical Structure](image)

**2-Octyl-4-(trifluoromethoxy)benzonitrile (7k):** Light yellow oil (48 mg, 81%, procedure A); $R_f$ 0.50 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65 (d, $J = 8.4$ Hz, 1H), 7.15 – 7.11 (m, 2H), 2.88 – 2.82 (m, 2H), 1.71 – 1.64 (m, 2H), 1.42 – 1.22 (m, 10H), 0.88 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.3, 150.0, 134.8, 122.2 (d, $^1$J$_{C-F}$ = 238.5 Hz), 121.6, 118.6, 117.3, 111.0, 34.9, 32.0, 30.9, 30.8, 29.5, 29.4, 22.9, 14.3; HRMS (ESI) Calcd for C$_{16}$H$_{21}$NOF$_3$ [M + H]$^+$ 300.1575, found 300.1577.

![Chemical Structure](image)

**4-(Methylthio)-2-octylbenzonitrile (7l):** Light yellow oil (37 mg, 71%, procedure A); $R_f$ 0.60 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48 (d, $J = 8.2$ Hz, 1H), 7.10 (d, $J = 1.6$ Hz, 1H), 7.07 (dd, $J = 8.2$, 1.9 Hz, 1H), 2.81 – 2.75 (m, 2H), 2.50 (s, 3H), 1.69 – 1.61 (m, 2H), 1.40 – 1.23 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.3, 145.9, 133.0, 126.1, 123.1, 118.6, 108.2, 34.9, 32.8, 31.1, 29.6, 29.5, 29.4, 22.9, 15.0, 14.3; HRMS (ESI) Calcd for C$_{16}$H$_{24}$NS [M + H]$^+$ 262.1629, found 262.1633.

![Chemical Structure](image)

**4-Fluoro-2-octylbenzonitrile (7m):** Light yellow oil (37 mg, 79%, procedure B); $R_f$ 0.58 (hexane/EtOAc = 10/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (dd, $J = 8.5$, 5.5 Hz, 1H), 7.04 – 6.95 (m, 2H), 2.86 – 2.80 (m, 2H), 1.70 – 1.62 (m, 2H), 1.40 – 1.23 (m, 10H), 0.88 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.2 (d, $^1$J$_{C-F}$ = 256.0 Hz), 150.6 (d, $^3$J$_{C-F}$ = 8.8 Hz), 135.2 (d, $^3$J$_{C-F}$ = 9.6 Hz), 117.7, 117.0 (d, $^2$J$_{C-F}$ = 22.3 Hz), 114.3 (d, $^2$J$_{C-F}$ = 22.8 Hz), 108.7, 34.8, 32.0, 30.8, 29.5, 29.4, 22.9, 14.3; HRMS (ESI) Calcd for C$_{15}$H$_{21}$NF [M + H]$^+$ 234.1658, found 234.1665.
5-Methyl-2-octylbenzonitrile (7n): Light yellow oil (35 mg, 77%, procedure B); Rf 0.61 (hexane/EtOAc = 10/1); 1H NMR (400 MHz, CDCl3): δ 7.40 (d, J = 0.6 Hz, 1H), 7.30 (dd, J = 7.9, 1.6 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 2.81 – 2.75 (m, 2H), 2.34 (s, 3H), 1.67 – 1.60 (m, 2H), 1.38 – 1.23 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 144.1, 136.3, 133.8, 133.2, 129.6, 118.6, 112.3, 34.4, 32.1, 31.2, 29.6, 29.5, 22.9, 20.9, 14.3; HRMS (ESI) Calcd for C16H24N [M + H]+ 230.1909, found 230.1916.

2-Octyl-5-(trifluoromethyl)benzonitrile (7o): Light yellow oil (34 mg, 61%, procedure A); Rf 0.60 (hexane/EtOAc = 10/1); 1H NMR (400 MHz, CDCl3): δ 7.86 (d, J = 1.5 Hz, 1H), 7.75 (dd, J = 8.3, 1.5 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 2.93 – 2.87 (m, 2H), 1.73 – 1.64 (m, 2H), 1.30 – 1.26 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 151.1, 130.4, 129.9 (q, 3J_C-F = 3.7 Hz), 129.5 (q, 3J_C-F = 3.2 Hz), 128.8 (q, 2J_C-F = 111.8 Hz), 123.4 (q, 1J_C-F = 272.3 Hz), 117.0, 113.5, 34.9, 32.0, 30.9, 29.5, 29.4, 22.9, 14.3; HRMS (ESI) Calcd for C16H21NF3 [M + H]+ 284.1626, found 284.1629.

4-Octylbenzo[cd][1,3]dioxole-5-carbonitrile (7p): Procedure A was applied. Silica gel chromatography (eluent: hexane/EtOAc = 50/1) of the crude product afforded a mixture of the title compound and its regioisomer 7p' as a light yellow oil (39 mg, 75%). The ratio of 7p and 7p' was determined to be 3:2 by 1H NMR analysis.
Rf 0.50 (hexane/EtOAc = 10/1); 1H NMR (400 MHz, CDCl3): δ 7.18 (d, J = 8.1 Hz, 1H for 7q), 6.96 (s, 1H for 7q' ), 6.74 (s, 1H for 7q' ), 6.72 (d, J = 8.1 Hz, 1H for 7q), 6.04 (s, 2H for 7q), 6.02 (s, 2H for 7q' ), 2.78 – 2.70 (m, 2H for each isomer), 1.68 – 1.60 (m, 2H for each isomer), 1.38 – 1.22 (m, 10H for each isomer), 0.88 (t, J = 6.7 Hz, 3H for each isomer); 13C NMR (100 MHz, CDCl3): δ 151.8, 150.9, 146.4, 146.2, 143.9, 128.7, 127.8, 118.6, 118.4, 111.5, 109.8,
HRMS (ESI) Calcd for C_{16}H_{22}NO_2 [M + H]^+ 260.1651, found 260.1645.

4'-{(Trimethylsilyl)}-[1,1'-biphenyl]-2-carbonitrile (7q): Light yellow oil (31 mg, 61%, procedure A); R_f 0.46 (hexane/EtOAc = 10/1); \^1H NMR (400 MHz, CDCl_3): \delta 7.79 – 7.76 (m, 1H), 7.67 – 7.62 (m, 3H), 7.57 – 7.51 (m, 3H), 7.47 – 7.42 (m, 1H), 0.32 (s, 9H); \^13C NMR (100 MHz, CDCl_3): δ 145.7, 141.5, 138.6, 134.1, 134.0, 133.1, 130.3, 128.2, 127.8, 119.0, 111.5, -0.9; HRMS (ESI) Calcd for C_{16}H_{18}NSi [M + H]^+ 252.1209, found 252.1213.

3'-Methyl-[1,1'-biphenyl]-2-carbonitrile (7r): Light yellow oil (24 mg, 61%, procedure B); R_f 0.45 (hexane/EtOAc = 10/1); \^1H NMR (400 MHz, CDCl_3): \delta 7.77 – 7.74 (m, 1H), 7.66 – 7.61 (m, 1H), 7.52 – 7.50 (m, 1H), 7.45 – 7.40 (m, 1H), 7.39 – 7.35 (m, 3H), 7.28 – 7.25 (m, 1H), 2.44 (s, 3H); \^13C NMR (100 MHz, CDCl_3): δ 145.9, 138.6, 138.4, 133.9, 133.0, 130.3, 129.7 (two signals overlapped), 128.8, 127.6, 126.1, 119.0, 111.5, 21.7; HRMS (ESI) Calcd for C_{14}H_{12}N [M + H]^+ 194.0970, found 194.0972.

3'-Methoxy-[1,1'-biphenyl]-2-carbonitrile (7s): Light yellow oil (24 mg, 58%, procedure B); R_f 0.31 (hexane/EtOAc = 10/1); \^1H NMR (400 MHz, CDCl_3): \delta 7.78 – 7.74 (m, 1H), 7.67 – 7.61 (m, 1H), 7.54 – 7.51 (m, 1H), 7.47 – 7.37 (m, 2H), 7.15 – 7.12 (m, 1H), 7.10 – 7.08 (m, 1H), 7.01 – 6.97 (m, 1H), 3.87 (s, 3H); \^13C NMR (100 MHz, CDCl_3): δ 159.9, 145.6, 139.7, 138.4, 134.0, 133.0, 130.3, 130.0, 127.8, 121.4, 114.7, 114.5, 111.6, 55.6; HRMS (ESI) Calcd for
C_{14}H_{12}NO [M + H]^+ 210.0919, found 210.0920.

4'-Methoxy-5-methyl-[1,1'-biphenyl]-2-carbonitrile (7t): Light yellow oil (27 mg, 60%, procedure B); R_f 0.36 (hexane/EtOAc = 10/1); ^1H NMR (400 MHz, CDCl3): δ 7.62 (d, J = 7.9 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.29 (s, 1H), 7.22 – 7.18 (m, 1H), 7.03 – 6.98 (m, 2H), 3.86 (s, 3H), 2.45 (s, 3H); ^13C NMR (100 MHz, CDCl3): δ 160.2, 145.3, 143.8, 133.9, 130.9, 130.8, 130.2, 128.1, 119.5, 114.4, 108.3, 55.6, 22.1; HRMS (ESI) Calcd for C_{15}H_{14}NO [M + H]^+ 224.1075, found 224.1077.

4',5-Dimethoxy-[1,1'-biphenyl]-2-carbonitrile (7u): Light yellow oil (27 mg, 57%, procedure A); R_f 0.23 (hexane/EtOAc = 10/1); ^1H NMR (400 MHz, CDCl3): δ 7.66 (d, J = 8.6 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.04 – 6.98 (m, 2H), 6.96 (d, J = 2.6 Hz, 1H), 6.90 (dd, J = 8.6, 2.5 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H); ^13C NMR (100 MHz, CDCl3): δ 162.9, 160.4, 147.5, 135.7, 130.8, 130.1, 119.6, 115.5, 114.4, 113.3, 103.2, 55.8, 55.6; HRMS (ESI) Calcd for C_{15}H_{14}NO_2 [M + H]^+ 240.1025, found 240.1015.

5-Fluoro-4'-methoxy-[1,1'-biphenyl]-2-carbonitrile (7v): White solid (24 mg, 54%, procedure A); R_f 0.34 (hexane/EtOAc = 10/1); M.p. 146-147 °C; ^1H NMR (400 MHz, CDCl3): δ 7.74 (dd, J = 8.6, 5.6 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.19 (dd, J = 9.5, 2.5 Hz, 1H), 7.10 (td, J = 8.2, 2.5 Hz, 1H), 7.05 – 7.00 (m, 2H), 3.87 (s, 3H); ^13C NMR (100 MHz, CDCl3): δ 165.1 (d, J_{C-F} = 249.0 Hz), 160.7, 148.5 (d, J_{C-F} = 7.6 Hz), 136.3 (d, J_{C-F} = 4.6 Hz), 130.1, 129.6, 118.6, 117.3 (d, J_{C-F} =...
$F = 22.9$ Hz), 114.9 (d, $^{2}J_{C\cdot F} = 22.9$ Hz), 114.6, 107.4, 55.6; HRMS (ESI) Calcd for $C_{14}H_{11}NOF$ [$M + H]^+$ 228.0825, found 228.0822.
Reaction of 1i with t-BuCH$_2$MgBr

Imine 1i (35 mg, 0.20 mmol) was placed in a J. Young NMR tube, and dissolved in [D$_8$]-THF (0.6 mL). After measurement of $^1$H and $^{13}$C NMR spectra, to this sample was added a THF solution of t-BuCH$_2$MgBr (0.20 mL, 1.5 M, 0.30 mmol) under nitrogen atmosphere at room temperature. The stopcock was closed and the resulting mixture was kept standing for 0.5 h. The sample was then subjected to $^1$H and $^{13}$C NMR measurements (Figure S1; the full spectra are attached to the bottom of this Supporting Information).

Figure S1. Imine/aromatic regions of $^1$H (left) and $^{13}$C (right) NMR spectra of 1i before (a) and after (b) the addition of t-BuCH$_2$MgBr.
References

$^1$H and $^{13}$C NMR Spectra

1b

1b
S49
$\text{t-Bu}$

3ag

$\text{NH}$

$\text{t-Bu}$

3ag
3ah

\[ \text{NH} \quad \text{t-Bu} \]

3ah

\[ \text{NH} \quad \text{t-Bu} \]
S77
3ka
r.r. = 4:1

3ka
r.r. = 4:1
3na

\[
\text{S85}
\]
S112
5la

S116
7f

7f

S123
S125
S137
1i (in [D₈]-THF)
1i

$\text{Me} - \text{NH} - \text{Me}$

$t$-Bu

$t$-BuCH$_2$MgBr (1.5 equiv)

1i

$t$-Bu

$\text{Me} - \text{NH} - \text{t-Bu}$

$t$-BuCH$_2$MgBr (1.5 equiv)