Supporting Information for

Rh-catalyzed Aminative Dearomatization of 2-Naphthols

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General methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

$^1$H and $^{13}$C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively), an Agilent instrument (400, 600 MHz and 100, 150 MHz, respectively) or a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. $^{19}$F NMR spectra were recorded on a Varian instrument, Agilent instrument (376 MHz) or a Bruker instrument (376 MHz) and internally referenced to CFCl$_3$. Data for $^1$H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant (s) in Hz, integration). Data for $^{13}$C NMR and $^{19}$F NMR are reported in terms of chemical shift (δ, ppm).
Optimization of reaction conditions

Table S1 DPH equivalent screening

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<th>3 (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<sup>a</sup> Reaction conditions: 1a (0.2 mmol), 2 (0.2X mmol), Rh$_2$(esp)$_2$ (1 mol%) in MeOH (2.0 mL) at rt. <sup>b</sup> Determined by $^1$H NMR using CH$_2$Br$_2$ (0.2 mmol) as an internal standard. <sup>c</sup> 2 mol% of Rh$_2$(esp)$_2$ was used.

Table S2 Base screening

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<th>entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>base</th>
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<td>2</td>
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Reaction conditions: \( \text{1a} \) (0.2 mmol), \( \text{2} \) (0.6 mmol), base (0.3 mmol), \( \text{Rh}_2(\text{esp})_2 \) (1 mol%) in MeOH (2.0 mL) at rt, \( ^b \) Determined by \( ^1 \text{H} \) NMR using \( \text{CH}_2\text{Br}_2 \) (0.2 mmol) as an internal standard.

**Table S3 Solvent screening**

\[
\begin{array}{ccc}
\text{entry}^a & \text{solvent} & \text{1a} \text{ (%)}^b & \text{3} \text{ (%)}^b \\
1 & \text{MeOH} & 7 & 57 \\
2 & \text{CH}_3\text{CH}_2\text{OH} & 10 & 50 \\
3 & \text{iPrOH} & 17 & 49 \\
4 & \text{iBuOH} & 27 & 37 \\
5 & \text{iAmyl-OH} & 43 & 26 \\
6 & \text{CF}_3\text{CH}_2\text{OH} & 3 & 49 \\
7 & \text{HFIP} & 47 & - \\
8 & \text{EtOAc} & 33 & 31 \\
9 & \text{CH}_3\text{CN} & 28 & 42 \\
\end{array}
\]
Reaction conditions: 1a (0.2 mmol), 2 (0.6 mmol), Rh$_2$(esp)$_2$ (1 mol%) in MeOH (2.0 mL) at rt, \textsuperscript{b} Determined by $^1$H NMR using CH$_2$Br$_2$ (0.2 mmol) as an internal standard. \textsuperscript{c} Isolated yields. \textsuperscript{d} CF$_3$CH$_2$OH (1.0 mL) and MeOH (1.0 mL) were used as co-solvent.

Table S4 catalyst screening

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$^a$ Reaction conditions: 1a (0.2 mmol), 2 (0.6 mmol), catalyst (1 mol%) in CF$_3$CH$_2$OH (1.0 mL) and MeOH (1.0 mL) at rt. $^b$ Determined by $^1$H NMR using CH$_2$Br$_2$ (0.2 mmol) as an internal standard.

**General procedure for the synthesis of substrates**

The synthesis of substituted naphthols was accomplished following the reported procedures.$^{1,3-7}$

![1a](image)

**1a.** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.48 (s, 1H), 7.45-7.40 (m, 1H), 7.33-7.29 (m, 1H), 4.88 (s, 1H), 2.52 (s, 3H), 2.42 (s, 3H).
$^{1b}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.49 (s, 1H), 7.45-7.41 (m, 1H), 7.33-7.30 (m, 1H), 4.92 (s, 1H), 2.80 (q, $J = 7.6$ Hz, 2H), 2.53 (s, 3H), 1.35 (t, $J = 7.6$ Hz, 3H).

$^{1c}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.51 (s, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.35-7.22 (m, 6H), 4.83 (s, 1H), 4.17 (s, 2H), 2.50 (s, 3H).

$^{1d}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 8.4$ Hz, 1H), 7.72 (s, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.49-7.45 (m, 1H), 7.37-7.33 (m, 1H), 5.77 (s, 1H), 2.58 (s, 3H).

$^{1e}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90-7.88 (m, 2H), 7.69-7.66 (m, 1H), 7.51-7.47 (m, 1H), 7.36-7.32 (m, 1H), 5.70 (s, 1H), 2.61 (s, 3H).

$^{1f}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (s, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.51-7.48 (m, 1H), 7.35-7.31 (m, 1H), 5.39 (s, 1H), 2.62 (s, 3H).
1g. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.60 (s, 1H), 7.54-7.44 (m, 6H), 7.37-7.34 (m, 1H), 5.33 (s, 1H), 2.61 (s, 3H).

1h. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.49 (s, 1H), 7.40-7.40 (m, 1H), 7.32-7.28 (m, 1H), 4.90 (s, 1H), 3.06 (q, $J = 7.6$ Hz, 2H), 2.43 (s, 3H), 1.28 (t, $J = 7.6$ Hz, 3H).

1i. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 8.4$ Hz, 1H), 7.43 (s, 1H), 7.40 (s, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 4.80 (s, 1H), 2.51 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H).

1j. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (s, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.44 (s, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 4.85 (s, 1H), 2.51 (s, 6H), 2.41 (s, 3H).
1k. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.51-7.47 (m, 1H), 7.36-7.32 (m, 1H), 7.06 (d, $J = 8.8$ Hz, 1H), 4.84 (s, 1H), 2.54 (s, 3H).

\[ \text{1k} \]

1l. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.50-7.47 (m, 1H), 7.35-7.31 (m, 1H), 7.06 (d, $J = 8.8$ Hz, 1H), 4.86 (s, 1H), 3.07 (q, $J = 7.6$ Hz, 2H), 1.29 (t, $J = 7.6$ Hz, 3H).

\[ \text{1l} \]

1m. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.45-7.41 (m, 1H), 7.34-7.31 (m, 1H), 7.26-7.14 (m, 5H), 7.11 (d, $J = 8.8$ Hz, 1H), 4.90 (s, 1H), 4.45 (s, 2H).

\[ \text{1m} \]

1n. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82-7.79 (m, 2H), 7.60-7.57 (m, 2H), 7.52-7.48 (m, 1H), 7.43-7.39 (m, 3H), 7.35-7.30 (m, 2H), 7.27-7.25 (m, 1H), 5.13 (s, 1H).

\[ \text{1n} \]

1o. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J = 9.2$ Hz, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.17 (dd, $J = 9.2$, 2.4 Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 4.74 (s, 1H), 3.90 (s, 3H), 2.51 (s, 3H).

\[ \text{1o} \]
1p. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.67-7.65 (m, 2H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 6.99 (d, $J = 8.8$ Hz, 1H), 4.81 (s, 1H), 2.53 (s, 3H), 2.51 (s, 3H).

1q. $^1H$ NMR (400 MHz, DMSO-d$_6$) $\delta$ 9.56 (s, 1H), 8.08 (s, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.79-7.77 (m, 3H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.51-7.47 (m, 2H), 7.38-7.34 (m, 1H), 7.19 (d, $J = 8.8$ Hz, 1H), 2.44 (s, 3H).

**General procedure for the aminative dearomatization of naphthols**

Naphthol derivative 1 (0.2 mmol, 1.0 equiv) was added to an oven-dried Schlenk tube, CF$_3$CH$_2$OH (1 mL) and MeOH (1 mL) were added under argon at room temperature. To this solution were added Rh$_2$(esp)$_2$ (1.5 mg, 0.002 mmol, 0.01 equiv) and DPH 2 (120 mg, 0.6 mmol, 3.0 equiv). After the reaction was complete (monitored by TLC), the reaction was quenched by saturated aqueous solution of NaHCO$_3$ (5 mL). The aqueous phase was extracted with ethyl acetate ($3 \times 10$ mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was then purified by silica gel column chromatography [PE/EtOAc = 5/1, then PE/EtOAc = 5/1 (1% Et$_3$N)] to afford the desired product 3.
3a: Yellow oil, 22.1 mg, 59% yield, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 8.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.30-7.27 (m, 1H), 7.24-7.23 (m, 2H), 2.04 (brs, 2H), 2.02 (s, 3H), 1.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 206.6, 145.4, 141.3, 131.1, 129.3, 129.2, 128.5, 127.5, 126.0, 60.9, 32.7, 15.8; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3359, 3294, 3044, 2968, 2923, 1653, 1438, 1361, 1262, 1091, 1026, 894, 819, 745; HRMS (ESI) calcd for C$_{12}$H$_{14}$NO ([M+H]$^+$): 188.1070. Found: 188.1064.

3b: Yellow oil, 24.6 mg, 61% yield, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 7.6 Hz, 1H), 7.38-7.34 (m, 1H), 7.31-7.25 (m, 2H), 7.17 (s, 1H), 2.54-2.34 (m, 2H), 1.96 (brs, 2H), 1.39 (s, 3H), 1.16 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 206.2, 145.2, 139.5, 136.7, 129.3, 128.6, 127.5, 125.9, 61.2, 32.5, 22.4, 12.6; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3358, 3296, 3048, 2959, 1659, 1448, 1378, 1255, 1084, 1019, 936, 881, 817, 758; HRMS (ESI) calcd for C$_{13}$H$_{16}$NO ([M+H]$^+$): 202.1226. Found: 202.1221.

3c: Yellow oil, 30.9 mg, 59% yield, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 7.6 Hz, 1H), 7.38-7.18 (m, 8H), 7.06 (s, 1H), 3.79 (AB, $J_{AB}$ = 16.0 Hz, 1H), 3.68 (BA, $J_{BA}$ = 16.0 Hz, 1H), 2.04 (brs, 2H), 1.35 (s, 3H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ 205.8, 145.4, 141.5, 138.9, 134.6, 129.6, 129.10, 129.08, 129.0, 128.5, 127.5, 126.4, 126.0, 61.4, 35.5, 32.6; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3357, 3297, 3039, 2915, 1656, 1500, 1439, 1374, 1321, 1258, 1086, 970, 894, 816, 750, 710; HRMS (ESI) calcd for C$_{15}$H$_{18}$NO ([M+H]$^+$): 264.1383. Found: 264.1376.
3d: Yellow oil, 20.9 mg, 50% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J$ = 8.0 Hz, 1H), 7.64 (s, 1H), 7.47-7.43 (m, 1H), 7.36-7.32 (m, 1H), 7.29-7.27 (m, 1H), 1.99 (brs, 2H), 1.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.5, 145.0, 142.5, 130.7, 129.1, 128.4, 128.06, 128.02, 126.6, 63.2, 32.8; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3359, 3298, 2920, 1675, 1598, 1496, 1444, 1341, 1221, 1146, 1083, 1023, 933, 839, 754; HRMS (ESI) calcd for C$_{11}$H$_{11}$ClNO ([M+H]$^+$): 208.0524. Found: 208.0519.

![Image of 3d](image_url)

3e: Yellow solid, 25.7 mg, 51% yield, m.p. 60-62 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (s, 1H), 7.87 (d, $J$ = 8.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.35-7.31 (m, 1H), 7.30-7.28 (m, 1H), 1.99 (brs, 2H), 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.6, 146.7, 145.4, 130.9, 129.1, 128.8, 128.0, 126.0, 63.1, 32.8; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3363, 2983, 2921, 2311, 2097, 1857, 1660, 1586, 1439, 1333, 1217, 1150, 1076, 915, 824, 767; HRMS (ESI) calcd for C$_{11}$H$_{11}$BrNO ([M+H]$^+$): 252.0019. Found: 252.0012.

![Image of 3e](image_url)

3f: Yellow solid, 27.0 mg, 45% yield, m.p. 96-98 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (s, 1H), 7.88 (d, $J$ = 8.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.34-7.30 (m, 1H), 7.26-7.25 (m, 1H), 2.12 (brs, 2H), 1.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.8, 154.1, 145.9, 131.0, 130.1, 128.9, 127.9, 126.5, 98.8, 62.1, 32.9; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3358, 3298, 2978, 2918, 2956, 2307, 2104, 1654, 1577, 1438, 1334, 1211, 1146, 1072, 1022, 892, 825, 758; HRMS (ESI) calcd for C$_{11}$H$_{11}$INO ([M+H]$^+$): 299.9880. Found: 299.9871.
**3g**: Yellow solid, 30.6 mg, 61% yield, m.p. 138-140 °C. $^1$H NMR (400 MHz, CDCl₃) δ 7.88 (d, $J = 8.0$ Hz, 1H), 7.54-7.51 (m, 3H), 7.44-7.31 (m, 6H), 2.18 (brs, 2H), 1.52 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 205.2, 145.6, 141.4, 135.5, 134.2, 130.1, 129.6, 129.2, 128.35, 128.32, 128.2, 127.7, 126.0, 62.3, 32.3; IR (thin film): $\nu_{\text{max}}$ (cm⁻¹) = 3371, 3310, 3044, 2921, 2861, 2308, 2105, 1658, 1458, 1358, 1292, 1205, 1066, 925, 828, 745, 709; HRMS (ESI) calcd for C₁₇H₁₆NO ([M+H]^+): 250.1226. Found: 250.1220.

**3h**: Yellow oil, 21.4 mg, 53% yield. $^1$H NMR (400 MHz, CDCl₃) δ 7.72 (d, $J = 8.0$ Hz, 1H), 7.38-7.34 (m, 1H), 7.30-7.28 (m, 1H), 7.23-7.21 (m, 2H), 2.14 (brs, 2H), 2.0 (s, 3H), 1.86-1.69 (m, 2H), 0.65 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 206.3, 143.9, 141.5, 132.0, 130.2, 129.0, 128.3, 127.5, 126.5, 64.2, 39.1, 15.6, 8.2; IR (thin film): $\nu_{\text{max}}$ (cm⁻¹) = 3356, 3043, 2928, 2866, 1652, 1442, 1368, 1322, 1260, 1029, 922, 816, 753; HRMS (ESI) calcd for C₁₃H₁₆NO ([M+H]^+): 202.1226. Found: 202.1221.

**3i**: Yellow oil, 22.2 mg, 55% yield. $^1$H NMR (400 MHz, CDCl₃) δ 7.68 (d, $J = 8.0$ Hz, 1H), 7.19-7.17 (m, 2H), 7.05 (s, 1H), 2.36 (s, 3H), 2.01 (d, $J = 1.2$ Hz, 3H), 1.81 (brs, 2H), 1.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 206.8, 142.5, 141.5, 137.2, 131.1, 130.1, 129.2, 129.1, 126.0, 60.7, 32.7, 21.0, 15.9; IR (thin film): $\nu_{\text{max}}$ (cm⁻¹) = 3572, 3355, 3290, 2921, 2868, 1651, 1502, 1440, 1368, 1269, 1100, 1026, 900, 818, 761; HRMS (ESI) calcd for C₁₃H₁₆NO ([M+H]^+): 202.1226. Found: 202.1221.
3j: Yellow oil, 21.2 mg, 53% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (s, 1H), 7.20 (s, 1H), 7.14-7.07 (m, 2H), 2.38 (s, 3H), 2.02-2.00 (m, 5H), 1.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.5, 145.3, 141.4, 139.7, 130.0, 128.5, 128.2, 126.8, 126.6, 60.9, 32.8, 21.6, 15.7; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3358, 3292, 2964, 2920, 2867, 1650, 1514, 1439, 1370, 1258, 1179, 1096, 1026, 964, 892, 810, 722; HRMS (ESI) calcd for C$_{13}$H$_{16}$NO ([M+H]$^+$): 202.1226. Found: 202.1221.

3k: Yellow oil, 33.3 mg, 64% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 7.6$ Hz, 1H), 7.46-7.42 (m, 2H), 7.32-7.31 (m, 2H), 6.20 (d, $J = 10.0$ Hz, 1H), 2.02 (brs, 2H), 1.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.3, 146.2, 145.1, 130.5, 129.4, 128.9, 127.6, 126.3, 123.5, 61.3, 32.6; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3356, 3294, 3048, 2971, 1660, 1448, 1225, 1146, 1077, 1023, 897, 815, 755, 679; HRMS (ESI) calcd for C$_{11}$H$_{12}$NO ([M+H]$^+$): 174.0913. Found: 174.0909.

3l: Yellow oil, 24.2 mg, 65% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 7.6$ Hz, 1H), 7.45-7.40 (m, 2H), 7.34-7.30 (m, 2H), 6.19 (d, $J = 10.0$ Hz, 1H), 1.88-1.71 (m, 5H), 0.69 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.3, 145.2, 145.1, 130.2, 129.8, 129.2, 127.5, 126.8, 124.4, 64.4, 38.9, 8.2; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3356, 3295, 3049, 2957, 1658, 1451, 1373, 1221, 1082, 950, 824, 755, 680; HRMS (ESI) calcd for C$_{12}$H$_{14}$NO ([M+H]$^+$): 188.1070. Found: 188.1065.
3m: Yellow oil, 28.9 mg, 58% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 7.2$ Hz, 1H), 7.42-7.38 (m, 1H), 7.33-7.29 (m, 1H), 7.22-7.07 (m, 5H), 6.68-6.61 (m, 2H), 6.03 (d, $J = 10.0$ Hz, 1H), 3.02 (AB, $J_{AB} = 12.8$ Hz, 1H), 2.96 (BA, $J_{BA} = 12.8$ Hz, 1H), 1.96 (brs, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.5, 144.9, 144.2, 134.5, 130.1, 130.04, 130.01, 129.2, 127.8, 127.6, 127.2, 126.8, 124.3, 65.3, 52.4; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3356, 3291, 3039, 2922, 2848, 1658, 1445, 1225, 1076, 1012, 820, 752, 690; HRMS (ESI) calcd for C$_{17}$H$_{16}$NO ([M+H]$^+$): 250.1226. Found: 250.1221.

3n: Yellow solid, 21 mg, 45% yield, m.p. 70-72 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 7.6$ Hz, 1H), 7.44-7.35 (m, 4H), 7.24-7.20 (m, 5H), 6.16 (d, $J = 10.0$ Hz, 1H), 2.42 (brs, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.2, 145.2, 144.8, 142.8, 130.6, 129.8, 129.3, 128.6, 128.5, 128.1, 127.7, 125.8, 124.1, 66.1; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3356, 3294, 3052, 2916, 2306, 2107, 1651, 1594, 1478, 1394, 1231, 1106, 1026, 972, 854, 826, 751, 684; HRMS (ESI) calcd for C$_{16}$H$_{14}$NO ([M+H]$^+$): 236.1070. Found: 236.1064.

3o: Yellow oil, 20.0 mg, 49% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 8.8$ Hz, 1H), 7.37 (d, $J = 9.6$ Hz, 1H), 6.97 (dd, $J = 8.8$, 2.8 Hz, 1H), 6.83 (d, $J = 2.4$ Hz, 1H), 6.20 (d, $J = 9.6$ Hz, 1H), 3.84 (s, 3H), 2.14 (brs, 2H), 1.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.3, 158.9, 144.9, 138.0, 129.9, 127.6, 124.0, 115.8, 114.5, 60.7, 55.4, 32.3; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2935, 2845, 2101, 1658, 1584, 1478, 1447,
1371, 1256, 1145, 1091, 1025, 808, 703; HRMS (ESI) calcd for C_{12}H_{11}O_{2} ([M-NH_{2}]^{+}): 187.0754. Found: 187.0755.

3p: Yellow oil, 17.5 mg, 47% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (s, 1H), 7.41 (d, $J = 10.0$ Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.14 (d, $J = 9.6$ Hz, 1H), 2.41 (s, 3H), 1.96 (brs, 2H), 1.41 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.4, 146.2, 145.1, 141.1, 129.4, 128.2, 127.1, 126.3, 122.5, 61.2, 32.7, 21.6; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3351, 3290, 3036, 2919, 2683, 2108, 1659, 1604, 1446, 1379, 1301, 1234, 1164, 1084, 1029, 896, 827, 679; HRMS (ESI) calcd for C$_{12}$H$_{14}$NO ([M+H]$^+$): 188.1070. Found: 188.1066.

3q: Yellow oil, 20.3 mg, 41% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.0$ Hz, 1H), 7.65 (dd, $J = 8.0$, 2.0 Hz, 1H), 7.61-7.58 (m, 2H), 7.52-7.44 (m, 4H), 7.40-7.38 (m, 1H), 6.24 (d, $J = 10.0$ Hz, 1H), 2.18 (brs, 2H), 1.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.1, 145.1, 145.0, 140.8, 139.9, 129.4, 129.2, 129.0, 128.1, 127.8, 127.0, 126.9, 124.0, 61.2, 32.5; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3363, 3300, 3044, 2918, 2859, 2312, 2103, 1652, 1465, 1364, 1296, 1239, 1176, 1077, 1025, 893, 821, 753, 690; HRMS (ESI) calcd for C$_{17}$H$_{16}$NO ([M+H]$^+$): 250.1226. Found: 250.1219.

**Gram-scale reaction**

\[
\begin{align*}
1a &+ \text{H}_2\text{N}-\text{O}_{\text{NO}_2} \rightarrow \text{Rh}_2(\text{esp})_2 (1 \text{ mol%}) \\
\text{CF}_2\text{CH}_2\text{OH}/\text{MeOH (1/1), rt} &\rightarrow \text{3a} \\
\text{870 mg} &\text{60% yield}
\end{align*}
\]

According to the general procedure, a gram-scale reaction was carried out. The
aminative dearomatization of 1a in 6.0 mmol scale gave the desired product 3a in 60% yield (670 mg).

Transformations of product 3a.

A flame-dried Schlenk tube was cooled down to room temperature under argon. To this tube were added 3a (56.2 mg, 0.30 mmol) and THF (2.0 mL). Then the reaction mixture was cooled to 0 °C, then NaHCO₃ (28 mg, 0.33 mmol) and CbzCl (47 μL, 0.33 mmol) were added. The resulting mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), the reaction mixture was quenched with H₂O and the aqueous phase was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was then purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford the desired product 4 as a yellow solid. 1090 mg, 93% yield. Two rotamers were observed by NMR. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 7.6 Hz, 1H), 7.38-6.99 (m, 9H), 6.01 (s, 1H), 4.98 and 4.66 (s, 2H), 2.03 (s, 3H), 1.39 (s, 3H).

A flame-dried Schlenk tube was cooled down to room temperature under argon. To this tube were added 3a (56.2 mg, 0.30 mmol), CeCl₃·7H₂O (157 mg, 0.42 mmol), and MeOH (3.0 mL). Then the reaction mixture was cooled to 0 °C, and NaBH₄ (23 mg, 0.60 mmol) was added. After completion (5 mins), the reaction was quenched by adding saturated NH₄Cl solution (3.0 mL). The mixture was diluted with H₂O (2.0 mL) and extracted with ethyl acetate (5 mL x 3). The combined ethyl acetate extracts were
washed with brine, dried over anhydrous Na$_2$SO$_4$ and filtrated. After the solvent was removed under reduced pressure, the crude product was purified by silica gel column chromatography [PE/EtOAc = 1:1 – DCM/MeOH = 5:1 (1% Et$_3$N)] to afford 5 as a grey sticky. 47 mg, 83% yield. $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.47 (d, $J = 6.8$ Hz, 1H), 7.33-7.27 (m, 2H), 7.14 (d, $J = 6.8$ Hz, 1H), 6.36 (s, 1H), 4.28 (s, 1H), 2.04 (s, 3H), 1.53 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 138.3, 135.8, 132.4, 128.4, 127.1, 126.4, 123.3, 123.0, 74.2, 58.7, 18.6, 18.2; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3341, 2905, 1596, 1490, 1439, 1376, 1283, 1244, 1129, 1081, 995, 945, 872, 835, 756, 647, 588, 548, 494, 424; HRMS (ESI) calcd for C$_{12}$H$_{16}$NO ([M+H]$^+$): 190.1226. Found: 190.1227.

The relative configuration of 5 is assigned via NOESY spectra.
Reference:


