Supporting Information for

Ru-Catalyzed Intermolecular Dearomatization Reaction of Indoles with Allylic Alcohols

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Table of Contents

General methods S2

Experimental details and characterization data S3-15

Copies of NMR Spectra S16-34
**General methods.** Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were freshly distilled according to standard methods prior to use.

$^1$H and $^{13}$C NMR spectra were recorded on a Varian instrument (300, 400 MHz and 75, 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for $^1$H NMR are recorded as follows: chemical shift ($\delta$, ppm), multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $m$ = multiplet or unresolved, $br$ = broad singlet, coupling constant(s) in Hz, integration). Data for $^{13}$C NMR are reported in terms of chemical shift ($\delta$, ppm).

**General procedure for ruthenium-catalyzed intermolecular dearomatization reaction of indoles with allylic alcohols:**

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added 3 (5.04 mg, 0.010 mmol, 5 mol%), TsOH·H$_2$O (3.8 mg, 0.020 mmol, 10 mol%), indole derivatives 1 (0.20 mmol, 100 mol%), allylic alcohol (0.80 mmol, 400 mol%), cyclohexane (2 mL). The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), the mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and filtrated. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product 4. The characterization data of the products are summarized below.
4aa. Colorless oil, 97% yield. $^1$H NMR (400 MHz, $d_6$-DMSO) $\delta$ 2.04-2.08 (m, 2H), 2.43-2.48 (m, 1H), 2.52-2.57 (m, 1H), 2.96-3.03 (m, 1H), 3.67 (s, 3H), 3.74-3.79 (m, 1H), 4.00-4.03 (m, 2H), 5.02-5.20 (m, 3H), 5.23-5.24 (m, 1H), 5.40 (s, 1H), 5.63-5.73 (m, 1H), 5.81-5.91 (m, 1H), 6.41 (d, $J = 7.6$ Hz, 1H), 6.62-6.65 (m, 1H), 7.01-7.07 (m, 2H).

4ba. Colorless oil, 80% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.24-1.32 (m, 3H), 1.98-2.10 (m, 2H), 2.39-2.45 (m, 1H), 2.51-2.56 (m, 1H), 3.04-3.11 (m, 1H), 3.75-4.19 (m, 5H), 5.04-5.11 (m, 3H), 5.15-5.22 (m, 1H), 5.33 and 5.44 (br, 1H), 5.59-5.70 (m, 1H), 5.79-5.87 (m, 1H), 6.36 (d, $J = 8.0$ Hz, 1H), 6.64-6.67 (m, 1H), 7.01 (d, $J = 7.2$ Hz, 1H), 7.05-7.09 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.7, 37.1, 37.5, 43.2, 43.4, 45.2, 48.6, 55.7, 56.9, 61.1, 61.2, 83.9, 84.3, 106.0, 115.7, 117.0, 117.3, 118.3, 122.7, 128.3, 132.1, 133.8, 134.2, 134.3, 150.0, 154.6, 155.5. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3076, 3055, 2978, 2877, 1697, 1641, 1605, 1489, 1463, 1412, 1379, 1328, 1308, 1264, 1246, 1207, 1159, 1105, 1086, 1032, 993, 914, 768, 739, 668; HRMS (ESI) calcd for C$_{19}$H$_{25}$N$_2$O$_2$ [M+H]$^+$: 313.1916. Found: 313.1912.

4ca. Colorless oil, 97% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.92-0.99 (m, 3H), 1.61-1.73 (m, 2H), 1.99-2.06 (m, 2H), 2.39-2.45 (m, 1H), 2.51-2.56 (m, 1H), 3.05-3.12 (m, 1H), 3.75-4.08 (m, 5H), 5.04-5.10 (m, 3H), 5.14-5.23 (m, 1H), 5.35 and 5.45 (br, 1H), 5.61-5.71 (m, 1H), 5.78-5.87 (m, 1H), 6.37 (d, $J = 7.2$ Hz, 1H), 6.62-6.65 (m, 1H), 7.01-7.07 (m, 2H).
6.63-6.67 (m, 1H), 7.01 (d, $J = 7.2$ Hz, 1H), 7.06 (dt, $J = 7.6$, 1.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 10.3, 10.4, 22.3, 37.2, 37.5, 43.2, 43.3, 45.1, 48.3, 48.6, 55.7, 56.8, 66.7, 67.0, 83.9, 84.3, 105.9, 106.0, 115.6, 117.0, 117.2, 118.3, 122.7, 128.2, 132.1, 133.8, 134.1, 134.3, 150.0, 154.7, 155.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3076, 3055, 2965, 2879, 1697, 1641, 1605, 1490, 1461, 1413, 1365, 1329, 1308, 1262, 1207, 1159, 1086, 1031, 991, 943, 914, 885, 767, 739, 668, 617; HRMS (ESI) calcd for C$_{20}$H$_{27}$N$_2$O$_2$ [M+H]$^+$: 327.2073. Found: 327.2053.

![Image](image1.png)

**4da.** Colorless oil, 94% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.10-2.18 (m, 2H), 2.44-2.62 (m, 2H), 3.13-3.31 (m, 1H), 3.93-4.12 (m, 3H), 5.06-5.24 (m, 4H), 5.49 and 5.54 (br, 1H), 5.63-5.73 (m, 1H), 5.79-5.89 (m, 1H), 6.41 (d, $J = 7.6$ Hz, 1H), 6.67-6.72 (m, 1H), 7.04 (d, $J = 7.2$ Hz, 1H), 7.08-7.22 (m, 4H), 7.32-7.39 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 37.0, 37.4, 43.2, 43.4, 45.5, 45.7, 48.66, 48.73, 55.9, 57.0, 84.3, 84.5, 106.2, 115.7, 116.1, 117.3, 117.6, 118.6, 121.6, 121.7, 122.8, 125.26, 125.31, 128.4, 129.2, 129.3, 131.9, 133.6, 133.7, 133.9, 134.2, 149.9, 151.0, 151.1, 152.5, 153.7. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3074, 2977, 2882, 1717, 1640, 1604, 1489, 1462, 1434, 1386, 1332, 1310, 1264, 1245, 1198, 1156, 1068, 1027, 993, 913, 873, 847, 787, 739, 687, 626; HRMS (ESI) calcd for C$_{23}$H$_{25}$N$_2$O$_2$ [M+H]$^+$: 361.1916. Found: 361.1904.

![Image](image2.png)

**4ea.** Colorless oil, 95% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.46 and 1.50 (s, 9H), 1.97-2.07 (m, 2H), 2.40-2.45 (m, 1H), 2.51-2.56 (m, 1H), 3.02-3.04 (m, 1H), 3.68-4.07 (m, 3H), 5.06-5.10 (m, 3H), 5.18 (d, $J = 17.2$ Hz, 1H), 5.29 and 5.42 (br,
1H), 5.60-5.70 (m, 1H), 5.77-5.86 (m, 1H), 6.34 (d, J = 8.0 Hz, 1H), 6.64-6.65 (m, 1H), 6.99-7.07 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 28.4, 37.2, 37.6, 43.3, 44.8, 45.4, 48.4, 48.6, 55.7, 56.8, 79.5, 80.1, 84.1, 84.4, 105.8, 115.4, 115.5, 116.8, 117.1, 118.2, 122.7, 128.2, 132.2, 134.0, 134.3, 134.5, 150.0, 150.1, 153.8, 154.6. IR (thin film): ν_max (cm⁻¹) = 2976, 2930, 2883, 1740, 1693, 1641, 1605, 1490, 1462, 1390, 1309, 1243, 1218, 1151, 1085, 1043, 1032, 992, 914, 888, 768, 739; HRMS (ESI) calcd for C21H29N2O2 [M+H]^+: 341.2229. Found: 341.2225.

4fa. Colorless oil, 88% yield. 1H NMR (400 MHz, CDCl3) δ 1.38-1.46 (m, 1H), 1.86-1.90 (m, 1H), 1.96-2.02 (m, 1H), 2.28-2.33 (m, 1H), 2.46 (s, 3H), 3.03-3.11 (m, 1H), 3.61-3.65 (m, 1H), 3.94-4.00 (m, 1H), 4.15-4.22 (m, 1H), 4.90-4.96 (m, 2H), 5.16 (d, J = 14.8 Hz, 1H), 5.23-5.28 (m, 2H), 5.34-5.45 (m, 1H), 5.82-5.91 (m, 1H), 6.38 (d, J = 8.0 Hz, 1H), 6.61-6.64 (m, 1H), 6.92 (d, J = 8.4 Hz, 1H), 7.04-7.08 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H). 13C NMR (100 MHz, CDCl3) δ 21.5, 38.3, 43.0, 46.6, 47.9, 57.0, 86.6, 105.9, 116.2, 117.2, 118.3, 122.7, 127.2, 128.4, 129.8, 130.9, 133.7, 137.0, 143.6, 149.8. IR (thin film): ν_max (cm⁻¹) = 3073, 2916, 1639, 1606, 1489, 1465, 1445, 1415, 1398, 1337, 1302, 1252, 1176, 1154, 1124, 1103, 1078, 1055, 991, 952, 915, 876, 841, 807, 734, 708, 662; HRMS (ESI) calcd for C23H27N2O2S [M+H]^+: 395.1793. Found: 395.1790.

4ga. Colorless oil, 91% yield. 1H NMR (400 MHz, CDCl3) δ 2.06-2.16 (m, 2H), 2.44-2.49 (m, 1H), 2.59-2.64 (m, 1H), 3.44-3.51 (m, 1H), 3.90-3.96 (m, 3H), 5.02-5.27 (m, 5H), 5.62-5.72 (m, 1H), 5.81-5.90 (m, 1H), 6.36 (d, J = 7.6 Hz, 1H),
6.64-6.68 (m, 1H), 7.04-7.09 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 40.0, 42.6, 47.1, 55.9, 66.7, 101.2, 105.2, 116.4, 117.1, 118.0, 123.2, 128.0, 132.4, 134.1, 134.3, 150.2.

IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3076, 2964, 2942, 2866, 2389, 1641, 1606, 1491, 1463, 1440, 1400, 1358, 1333, 1310, 1260, 1164, 1014, 949, 916, 871, 797, 740, 703, 664; HRMS (ESI) calcd for C$_{16}$H$_{20}$NO [$\text{M+H}^+$]: 242.1545. Found: 242.1540.

4ha. Colorless oil, 88% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.05-2.16 (m, 2H), 2.42-2.48 (m, 1H), 2.57-2.62 (m, 1H), 3.46-3.52 (m, 1H), 3.74 (s, 3H), 3.85-3.88 (m, 2H), 3.92-3.96 (m, 1H), 5.03-5.28 (m, 5H), 5.63-5.74 (m, 1H), 5.82-5.91 (m, 1H), 6.28 (d, $J$ = 8.4 Hz, 1H), 6.64 (dd, $J$ = 8.4, 2.4 Hz, 1H), 6.70 (d, $J$ = 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 39.8, 42.4, 48.0, 56.0, 56.1, 66.7, 101.9, 105.5, 111.1, 112.1, 116.4, 118.1, 134.0, 134.5, 144.6, 152.4. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3076, 2975, 2936, 2866, 1669, 1641, 1596, 1492, 1434, 1396, 1357, 1333, 1283, 1258, 1218, 1164, 1123, 1035, 1012, 951, 915, 883, 795, 747, 701, 653; HRMS (ESI) calcd for C$_{17}$H$_{22}$NO$_2$ [$\text{M+H}^+$]: 272.1651. Found: 272.1652.

4ia. Red oil, 94% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.34-1.44 (m, 1H), 1.54-1.63 (m, 1H), 1.72-1.79 (m, 1H), 1.94-2.00 (m, 1H), 2.26-2.39 (m, 2H), 3.42-3.48 (m, 1H), 3.61-3.67 (m, 1H), 3.82-3.84 (m, 2H), 4.77 (s, 1H), 5.02 (dd, $J$ = 16.8, 9.6 Hz, 2H), 5.17 (d, $J$ = 11.6 Hz, 1H), 5.29 (dd, $J$ = 17.2, 2.0 Hz, 1H), 5.64-5.74 (m, 1H), 5.86-5.95 (m, 1H), 6.49 (d, $J$ = 7.6 Hz, 1H), 6.69-6.72 (m, 1H), 6.98 (d, $J$ = 6.8 Hz, 1H), 7.07-7.11 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.7, 28.5, 43.3, 45.2, 47.0, 60.6, 95.9, 106.7, 116.4, 117.6, 117.8, 122.5, 127.7, 133.2, 134.1,
$\nu_{\text{max}}$ (cm$^{-1}$) = 3075, 2960, 2922, 2855, 1640, 1607, 1482, 1462, 1438, 1416, 1382, 1353, 1333, 1307, 1259, 1222, 1159, 1072, 1022, 956, 915, 863, 796, 739, 705; HRMS (ESI) calcd for C$_{17}$H$_{22}$NO $[\text{M+H}]^+$: 256.1701. Found: 256.1698.

$\delta$ 1.40-1.51 (m, 2H), 1.54-1.66 (m, 2H), 1.89 (dd, $J = 14.0$, 7.6 Hz, 1H), 1.99-2.05 (m, 1H), 2.25 (d, $J = 7.6$ Hz, 2H), 3.42-3.48 (m, 2H), 3.86-3.88 (m, 2H), 4.77 (s, 1H), 4.96-5.01 (m, 2H), 5.14-5.17 (m, 1H), 5.24-5.29 (m, 1H), 5.52-5.62 (m, 1H), 5.82-5.92 (m, 1H), 6.42 (d, $J = 7.6$ Hz, 1H), 6.64-6.68 (m, 1H), 6.87-6.91 (m, 1H), 7.05-7.09 (m, 1H). $\delta$ 23.9, 31.6, 33.5, 46.0, 52.8, 65.8, 100.3, 104.4, 116.5, 116.67, 116.72, 117.8, 123.3, 127.5, 132.9, 134.1, 134.2, 149.3. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3075, 3054, 2977, 2928, 2857, 2361, 1640, 1605, 1490, 1463, 1438, 1416, 1389, 1359, 1302, 1260, 1242, 1167, 1090, 1060, 1027, 993, 915, 800, 738, 698, 665; HRMS (ESI) calcd for C$_{15}$H$_{24}$NO $[\text{M+H}]^+$: 270.1858. Found: 270.1847.

$\delta$ 2.43-2.54 (m, 2H), 2.89 (s, 2H), 3.91-4.04 (m, 2H), 5.10-5.15 (m, 2H), 5.22-5.35 (m, 2H), 5.61-5.72 (m, 2H), 5.85-5.95 (m, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.80 (t, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 1H), 7.14-7.18 (m, 1H). $\delta$ 39.9, 41.2, 47.5, 51.8, 102.0, 107.6, 117.8, 119.3, 119.6, 123.4, 129.1, 132.0, 132.2, 132.9, 147.5, 174.8. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3077, 2963, 2915, 2855, 1769, 1641, 1606, 1487, 1463, 1439, 1417, 1398, 1340, 1289, 1261, 1216, 1161, 1100, 1045, 1008, 898, 849, 797, 743, 670.

4la. Colorless oil, 91% yield. ¹H NMR (300 MHz, CDCl₃) δ 2.34-2.47 (m, 2H), 2.81 (s, 2H), 3.65 (dd, J = 16.8, 6.0 Hz, 1H), 3.84 (dd, J = 16.5, 4.8 Hz, 1H), 4.12 (d, J = 15.3 Hz, 1H), 4.76 (s, 1H), 4.98-5.16 (m, 5H), 5.46-5.60 (m, 1H), 5.71-5.84 (m, 1H), 6.51 (d, J = 7.8 Hz, 1H), 6.78 (t, J = 7.8 Hz, 1H), 7.05 (d, J = 6.9 Hz, 1H), 7.09-7.15 (m, 1H), 7.20-7.36 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 42.0, 43.6, 43.8, 49.3, 52.4, 85.3, 109.1, 117.3, 119.3, 119.5, 123.2, 127.5, 127.6, 128.6, 128.7, 132.7, 134.0, 134.7, 136.2, 149.3, 173.1. IR (thin film): ν_max (cm⁻¹) = 3072, 3029, 2977, 2918, 1689, 1641, 1605, 1487, 1461, 1416, 1356, 1332, 1291, 1261, 1201, 1154, 1094, 1063, 1028, 996, 921, 801, 744, 702; HRMS (ESI) calcd for C₂₃H₂₅N₂O [M⁺]: 345.1967. Found: 345.1954.

4ma. Colorless oil, 90% yield. ¹H NMR (300 MHz, CDCl₃) δ 2.03-2.18 (m, 2H), 2.43-2.50 (m, 1H), 2.56-2.63 (m, 1H), 2.91 (s, 3H), 3.40-3.48 (m, 1H), 3.91-3.97 (m, 1H), 5.03-5.11 (m, 2H), 5.15 (s, 1H), 5.63-5.77 (m, 1H), 6.36 (d, J = 7.8 Hz, 1H), 6.66 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.08-7.13 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 30.8, 39.7, 42.3, 56.0, 67.0, 102.6, 104.8, 117.1, 117.9, 123.0, 128.2, 132.6, 134.3, 151.1. IR (thin film): ν_max (cm⁻¹) = 3052, 2967, 2926, 2869, 1640, 1607, 1493, 1444, 1429, 1388, 1357, 1331, 1301, 1258, 1228, 1155, 1120, 1015, 957, 915, 876, 798, 739, 698, 653; HRMS (ESI) calcd for C₁₄H₁₈NO [M+H]⁺: 216.1388. Found: 216.1383.
4gb. Colorless oil, 67% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.13-2.24 (m, 2H), 2.60-2.66 (m, 1H), 2.76-2.82 (m, 1H), 3.50-3.56 (m, 1H), 3.97-4.01 (m, 1H), 4.07-4.08 (m, 2H), 5.36 (s, 1H), 6.04-6.20 (m, 2H), 6.43-6.46 (m, 2H), 6.52-6.57 (m, 2H), 6.67-6.71 (m, 1H), 7.07-7.11 (m, 2H), 7.18-7.24 (m, 5H), 7.25-7.27 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 40.1, 41.8, 46.5, 56.4, 66.9, 101.2, 105.4, 117.4, 123.3, 125.8, 126.0, 126.1, 126.3, 127.2, 127.3, 128.3, 128.4, 128.5, 131.6, 132.4, 133.0, 136.8, 137.3, 150.2. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3079, 3054, 3025, 2965, 2922, 2865, 1949, 1878, 1805, 1735, 1603, 1489, 1463, 1445, 1398, 1358, 1305, 1261, 1157, 1069, 1042, 1012, 963, 914, 872, 803, 736, 692; HRMS (ESI) calcd for C$_{28}$H$_{28}$NO [M+H]$^+$: 394.2171. Found: 394.2161.

4gd. Colorless oil, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.62-1.64 (m, 3H), 1.67-1.70 (m, 3H), 2.01-2.15 (m, 2H), 2.38 (dd, $J$ = 14.0, 8.4 Hz, 1H), 2.49-2.54 (m, 1H), 3.43-3.49 (m, 1H), 3.82-3.85 (m, 2H), 3.90-3.95 (m, 1H), 5.23 (s, 1H), 5.26-5.34 (m, 1H), 5.42-5.54 (m, 2H), 5.61-5.71 (m, 1H), 6.36 (d, $J$ = 8.0 Hz, 1H), 6.63-6.67 (m, 1H), 7.01-7.09 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 17.7, 18.0, 39.9, 41.3, 46.3, 56.1, 66.7, 101.0, 105.1, 116.9, 123.2, 126.7, 126.8, 127.5, 127.9, 128.5, 132.9, 150.3. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3025, 2965, 2918, 2859, 1604, 1488, 1459, 1443, 1398, 1379, 1356, 1299, 1259, 1226, 1160, 1120, 1046, 1009, 961, 915, 878, 799, 737, 666, 628; HRMS (ESI) calcd for C$_{18}$H$_{24}$NO [M+H]$^+$: 270.1858. Found: 270.1847.
4naa. Yellow solid, 42% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.11-1.26 (m, 1H), 1.35-1.51 (m, 1H), 1.66-1.87 (m, 2H), 2.18-2.23 (m, 1H), 2.35-2.39 (m, 1H), 2.51-2.67 (m, 3H), 2.86-2.91 (m, 1H), 4.85-4.98 (m, 2H), 5.11-5.25 (m, 1H), 7.16-7.21 (m, 1H), 7.26-7.35 (m, 2H), 7.59 (d, $J = 7.5$ Hz, 1H).

4nab. Yellow oil, 49% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.84-1.97 (m, 4H), 2.62-2.75 (m, 4H), 4.62 (dd, $J = 3.0$, 1.8 Hz, 2H), 4.88 (dd, $J = 17.1$, 1.2 Hz, 1H), 5.09 (dd, $J = 10.5$, 1.5 Hz, 1H), 5.85-5.97 (m, 1H), 7.03-7.15 (m, 2H), 7.22 (d, $J = 8.1$ Hz, 1H), 7.47 (d, $J = 7.2$ Hz, 1H).

4oa. Yellow oil, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.28-1.39 (m, 1H), 1.62-1.70 (m, 1H), 1.78-1.85 (m, 1H), 1.91-1.95 (m, 2H), 2.03-2.09 (m, 1H), 2.38 (s, 1H), 2.56 (d, $J = 7.6$ Hz, 2H), 3.73-3.87 (m, 2H), 5.07-5.14 (m, 2H), 5.18-5.23 (m, 2H), 5.82-5.91 (m, 1H), 6.15-6.18 (m, 1H), 6.69-6.77 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 22.5, 37.8, 40.5, 40.7, 45.5, 55.6, 104.9 ($J = 7.8$ Hz), 106.4, 110.8 ($J = 23.3$ Hz), 113.3 ($J = 22.8$ Hz), 115.5, 118.2, 134.9 ($J = 7.2$ Hz), 135.4, 135.9, 144.7, 156.1 ($J = 232.8$ Hz). R (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3416, 3076, 2956, 2870, 1707, 1640, 1609, 1491, 1442, 1417, 1389, 1355, 1287, 1258, 1181, 1147, 1079, 1025, 1002, 917, 865, 801, 746, 711, 680; HRMS (ESI) calcd for C$_{17}$H$_{20}$FNO $[M+H]^+$: 274.1607. Found: 274.1608.
4pa. Yellow oil, 87% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.25-1.39 (m, 1H), 1.60-1.69 (m, 1H), 1.76-1.84 (m, 1H), 1.87-1.97 (m, 2H), 2.02-2.08 (m, 1H), 2.37 (s, 1H), 2.56 (d, $J = 9.2$ Hz, 2H), 3.70-3.87 (m, 2H), 3.74 (s, 3H), 5.04-5.13 (m, 2H), 5.16-5.25 (m, 2H), 5.67-5.78 (m, 1H), 5.84-5.93 (m, 1H), 6.21 (d, $J = 8.4$ Hz, 1H), 6.60 (dd, $J = 8.4$, 2.4 Hz, 1H), 6.67 (d, $J = 2.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.5, 37.5, 40.5, 40.6, 45.7, 55.7, 56.0, 105.1, 106.3, 111.1, 111.7, 115.2, 117.8, 135.1, 135.8, 136.3, 143.0, 152.2. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2963, 1411, 1260, 1090, 1019, 866, 798, 679; HRMS (ESI) calcd for C$_{18}$H$_{24}$NO$_2$ [M+H]$^+$: 286.1807. Found: 286.1810.

A gram-scale synthesis of 4aa.

A 50 mL flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added 3 (25.2 mg, 1.0 mol%), TsOH$\cdot$H$_2$O (19.0 mg, 2.0 mol%), Indole derivatives 1a (1.09 g, 5.0 mmol), allyl alcohol 2a (1.16 g, 40 mmol), cyclohexane (10 mL). The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and filtrated. The solvent was removed under reduced pressure, the residue was purified by column chromatography (PE/EA = 10/1) to afford the desired product 4aa (1.48 g, 99% yield).

Concise synthesis of debromoflustramine B
A 25 mL flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask was added 4aa (89.4 mg, 0.30 mmol). The vessel was placed under vacuum and the atmosphere exchanged with argon three times before the addition of CH2Cl2 (5 mL) and 2-methyl-2-buten (210.0 mg, 3.00 mmol). Then the mixture was heated to 40 °C before Grubbs II (25.5 mg, 0.03 mmol) was added. Then, the reaction mixture was stirred at 40 °C. After the reaction was almost complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na2SO4, and filtrated. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (PE/EA = 15/1) to afford the desired product 5aa1 as a colorless liquid (85.0 mg, 80% yield). Colorless oil, 80% yield. Analytical data for 5aa: 1H NMR (300 MHz, CDCl3) δ 1.55 (s, 3H), 1.64-1.75 (m, 9H), 2.02 (br s, 2H), 2.38 (d, J = 7.2 Hz, 2H), 3.01-3.10 (m, 1H), 3.70-4.21 (m, 6H), 5.04 (s, 1H), 5.14 (s, 1H), 5.23-5.34 (m, 1H), 6.35-6.37 (m, 1H), 6.61-6.66 (m, 1H), 6.97 (d, J = 7.2 Hz, 1H), 7.03-7.08 (m, 1H).

A flame-dried 25mL round bottom flask was cooled to room temperature and filled with argon. To this flask was added LiAlH4 (22.8 mg, 0.6 mmol), the atmosphere exchanged with argon three times before the addition of THF (10 mL) and the slow addition of 5aa (59.6 mg, 0.20 mmol). After the reaction was complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na2SO4, and filtrated. The solvent was removed under reduced pressure, the residue was purified by column chromatography (PE/EA = 1/2) to afford the desired product 6aa[1] as a
colorless liquid (60.8 mg, 98% yield). Analytical data for 6aa: $^1$H NMR (300 MHz, CDCl$_3$) δ 1.58 (s, 3H), 1.65 (s, 3H), 1.70 (s, 3H), 1.71 (s, 3H), 1.87-1.94 (m, 1H), 2.00-2.10 (m, 1H), 2.42 (d, $J = 6.9$ Hz, 2H), 2.48 (s, 3H), 2.52-2.60 (m, 1H), 2.63-2.70 (m, 1H), 3.76-3.84 (m, 1H), 3.89-3.96 (m, 1H), 4.26 (s, 1H), 4.94-4.99 (m, 1H), 5.14-5.19 (m, 1H), 6.39-6.44 (m, 1H), 6.64 (t, $J = 6.9$ Hz, 1H), 6.96 (d, $J = 6.9$ Hz, 1H), 7.00-7.06 (m, 1H).

Mechanistic investigation

The reaction of 1a with 2a was monitored by the HPLC analysis [Waters Spherisorb ® 5um Silica (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, $\nu$ = 1.0 mL·min$^{-1}$, $\lambda = 230$ nm, t (4aa) = 3.81 min, t (7aa) = 4.93 min, t (8aa) = 6.13 min, t (1a) = 11.08 min]. At first, substrate 1a, product 4aa and the two intermediates 7aa and 8aa were synthesized respectively, and then mixed together in an equivalent amount. After obtaining the integration ratio of different compounds, we can use HPLC to obtain the relative molar ratio of four compounds. The results analyzed by HPLC were showed in the following figure:
At the very beginning of the reaction, a large quantity of 7aa and a small amount of 8aa were generated. As the reaction proceeded, 7aa was rapidly consumed by the allylic amination reaction, while it took eight hours for 8aa to reach a full conversion.

**General procedure for ruthenium-catalyzed intermolecular enantioselective dearomatization reaction of indoles with allylic alcohols**:

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added 3 (5.04 mg, 0.010 mmol, 5 mol%), L* (0.01 mmol, 5 mol%) and CH₃CN (1 mL). The reaction mixture was stirred at room temperature for one hour. After that, TsOH·H₂O (3.8 mg, 0.020 mmol, 10 mol%), indole derivatives 1a (0.20 mmol, 100 mol%), allyl alcohol 2a (0.80 mmol, 400 mol%), and another 1 mL CH₃CN were added to the flask. The reaction mixture was stirred at room temperature until the reaction was complete (monitored by TLC). Then, the mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and filtrated. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product 4aa. The preliminary results for the enantioselective synthesis are summarized below.
Reaction conditions: 1a (0.2 mmol), allyl alcohol 2a (0.8 mmol), 3 (5 mol%), L* (5 mol%), TsOH·H2O (10 mol%) in CH3CN at room temperature. Isolated yield. Determined by HPLC analysis [column: Phenomenex Lu X 5u Amylose-2 (0.46 cm x 25 cm), n-hexane/2-propanol = 50/1, v = 0.51 mL·min⁻¹, λ = 254 nm].

References


Copies of NMR Spectra

Compound 4aa’s $^1$H NMR Spectra

In $d_6$-DMSO (110°C)

In CDCl$_3$ (rt)
Compound 4ba’s $^1$H NMR Spectra

Compound 4ba’s $^{13}$C NMR Spectra
Compound 4ca’s $^1$H NMR Spectra

Chemical Formula: C$_{24}$H$_{26}$N$_5$O$_2$
Exact Mass: 526.1984

Compound 4ca’s $^{13}$C NMR Spectra

Chemical Formula: C$_{24}$H$_{26}$N$_5$O$_2$
Exact Mass: 526.1984
Compound 4da’s $^1$H NMR Spectra

![1H NMR Spectra of Compound 4da](image1)

Chemical Formula: C$_2$H$_5$N$_2$O$_4$
Exact Mass: 360.1438

Compound 4da’s $^{13}$C NMR Spectra

![13C NMR Spectra of Compound 4da](image2)

Chemical Formula: C$_2$H$_5$N$_2$O$_4$
Exact Mass: 360.1438
Compound 4ea’s $^1$H NMR Spectra

Compound 4ea’s $^{13}$C NMR Spectra
Compound 4fa’s $^1$H NMR Spectra

Compound 4fa’s $^{13}$C NMR Spectra
Compound 4ga's $^1$H NMR Spectra

Chemical formula: $C_{44}H_{13}NO$
Exact Mass: 241.1407

Compound 4ga's $^{13}$C NMR Spectra

Chemical formula: $C_{44}H_{13}NO$
Exact Mass: 241.1407
Compound 4ha’s $^1$H NMR Spectra

Chemical Formula: C_{13}H_{18}NO_3
Exact Mass: 231.1572

Compound 4ha’s $^{13}$C NMR Spectra

Chemical Formula: C_{13}H_{18}NO_3
Exact Mass: 231.1572
Compound 4ia’s $^1$H NMR Spectra

Chemical formula: C$_{22}$H$_{24}$N$_2$O
Exact Mass: 355.1629

Compound 4ia’s $^{13}$C NMR Spectra

Chemical formula: C$_{22}$H$_{24}$N$_2$O
Exact Mass: 355.1629
Compound 4ja's $^1$H NMR Spectra

Compound 4ja's $^{13}$C NMR Spectra
Compound 4ka’s $^1$H NMR Spectra

Chemical Formula: C$_{12}$H$_{13}$NO$_3$
Exact Mass: 255.1259

Compound 4ka’s $^{13}$C NMR Spectra

Chemical Formula: C$_{12}$H$_{13}$NO$_3$
Exact Mass: 255.1259
Compound 4la’s $^1$H NMR Spectra

Compound 4la’s $^{13}$C NMR Spectra
Compound 4ma’s $^1$H NMR Spectra

Chemical formula: C_{14}H_{15}NO
Exact mass: 216.1310

Compound 4ma’s $^{13}$C NMR Spectra

Chemical formula: C_{14}H_{15}NO
Exact mass: 216.1310
Compound 4gb's $^1$H NMR Spectra

Compound 4gb's $^{13}$C NMR Spectra
Compound 4gd’s $^1$H NMR Spectra

Compound 4gd’s $^{13}$C NMR Spectra
Compound 4\textit{naa}'s $^1$H NMR Spectra

\begin{center}
\includegraphics[width=\textwidth]{nmaa_nmr.png}
\end{center}

Chemical Formula: C$_{18}$H$_{27}$N
Exact Mass: 211.1961

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Compound 4\textit{nab}'s $^1$H NMR Spectra

\begin{center}
\includegraphics[width=\textwidth]{nmaa_nmr.png}
\end{center}

Chemical Formula: C$_{18}$H$_{27}$N
Exact Mass: 211.1961
Compound 4oa’s $^1$H NMR Spectra

![Diagram of Compound 4oa's $^1$H NMR Spectra]

Compound 4oa’s $^{13}$C NMR Spectra

![Diagram of Compound 4oa's $^{13}$C NMR Spectra]
Compound 4pa’s $^1$H NMR Spectra

Chemical Formula: C$_{20}$H$_{15}$NO$_2$
Exact Mass: 285.1729

Compound 4pa’s $^{13}$C NMR Spectra

Chemical Formula: C$_{20}$H$_{15}$NO$_2$
Exact Mass: 285.1729
Compound 5aa’s $^1$H NMR Spectra

Compound 6aa’s $^1$H NMR Spectra