Supporting Information for

Gold-Catalyzed Intramolecular Dearomatization Reactions of Indoles for the Synthesis of Spiroindolenines and Spiroindolines

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1. 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 NMR spectrum were recorded on a Varian (400 MHz) or Agilent instrument (400 MHz or 600 MHz) and internally referenced to tetramethylsilane signal or residual solvent signals. $^{13}$C NMR spectrum were recorded on a Varian (100 MHz) or Agilent instrument (100 MHz) and internally referenced to residual solvent signals. $^{19}$F NMR spectrum were recorded on a Varian or Agilent instrument (376 MHz) and referenced relative to CFCl$_3$. Data for $^1$H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, 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).

Compound 1 and compound 4 were prepared following the known procedures.1,2,3
2. Experimental details and characterization data

2.1 Characterization data of indole derivatives (1, 4)

1a: (1a was purified by PE/EtOAc = 5:1) white solid, 6.73 g, 73% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (brs, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.27-7.25 (m, 2H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.14-7.10 (m, 2H), 4.18 (d, $J = 2.4$ Hz, 2H), 3.52 (t, $J = 7.6$ Hz, 2H), 3.08 (t, $J = 7.6$ Hz, 2H), 2.40 (s, 3H), 2.08-2.06 (m, 1H).

1b: (1b was purified by PE/EtOAc = 5:1) white solid, 1.64 g, 76% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (brs, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 7.2$ Hz, 1H), 7.8-7.26 (m, 3H), 7.17-7.09 (m, 2H), 4.22 (d, $J = 1.2$ Hz, 2H), 3.42 (t, $J = 8.4$ Hz, 2H), 3.05 (t, $J = 8.4$ Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H), 2.13 (s, 1H).

1c: (1c was purified by PE/EtOAc = 5:1) yellow solid, 0.52 g, 30% yield, M.P. = 99-102 $^\circ$C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84-7.81 (m, 2H), 7.79 (brs, 1H), 7.56-7.51 (m, 2H), 7.48-7.443 (m, 2H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.14-7.06 (m, 2H), 4.19 (d, $J = 2.4$ Hz, 2H), 3.42-3.38 (m, 2H), 3.05-3.01 (m, 2H), 2.40 (s, 3H), 2.05 (t, $J = 2.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.9, 135.1, 132.6, 131.9, 128.8, 128.3, 127.5, 121.1, 119.4, 117.7, 110.2, 107.8, 76.7, 73.7, 46.9, 37.0, 23.7, 11.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3380, 3258, 2905, 2384, 2322, 2117, 1587, 1461, 1440, 1326, 1157, 1091, 1024, 907, 877, 839, 730, 687, 617, 564, 540, 426; HRMS (ESI) calcd for C$_{20}$H$_{24}$N$_3$O$_2$S [M+NH$_4$]$^+$: 370.1584. Found: 370.1585.
**1d:** (1d was purified by PE/EtOAc = 4:1) yellow solid, 2.41 g, 69% yield, M.P. = 141-143 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.83 (brs, 1H), 7.67 (d, \(J = 8.8\) Hz, 2H), 7.57 (d, \(J = 8.8\) Hz, 2H), 7.51 (d, \(J = 7.6\) Hz, 1H), 7.27 (d, \(J = 7.2\) Hz, 1H), 7.15-7.08 (m, 2H), 4.19 (d, \(J = 2.4\) Hz, 2H), 3.42-3.38 (m, 2H), 3.05-3.01 (m, 2H), 2.39 (s, 3H), 2.11 (t, \(J = 2.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 137.8, 135.1, 132.0, 131.9, 129.0, 128.2, 127.6, 121.1, 119.4, 117.6, 110.3, 107.4, 76.4, 74.0, 46.8, 36.9, 23.5, 11.5. IR (thin film): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3380, 3267, 2922, 2116, 2091, 1572, 1459, 1331, 1157, 1089, 1004, 890, 820, 742, 666, 614, 566, 540; Anal. calcd for C\(_{20}\)H\(_{19}\)BrN\(_2\)O\(_2\)S: C, 55.69; H, 4.44; Found: C, 55.54; H, 4.55.

**1e:** (1e was purified by PE/EtOAc = 2:1) yellow solid, 1.31 g, 76% yield, M.P. = 128-131 °C. \(^1\)H NMR (400 MHz, \(d_6\)-DMSO) δ 10.77 (brs, 1H), 8.27 (d, \(J = 8.8\) Hz, 2H), 7.96 (d, \(J = 8.8\) Hz, 2H), 7.38 (d, \(J = 7.6\) Hz, 1H), 7.19 (d, \(J = 7.6\) Hz, 1H), 6.98-6.90 (m, 2H), 4.30 (d, \(J = 2.0\) Hz, 2H), 3.36 (t, \(J = 8.4\) Hz, 2H), 3.20 (t, \(J = 2.4\) Hz, 1H), 2.93 (t, \(J = 8.4\) Hz, 2H), 2.32 (s, 3H). \(^{13}\)C NMR (100 MHz, \(d_6\)-DMSO) δ 150.1, 144.5, 135.7, 133.0, 129.1, 128.4, 124.8, 120.6, 118.8, 117.5, 111.0, 106.5, 77.6, 77.1, 47.6, 37.0, 23.3, 11.7. IR (thin film): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3426, 3299, 3107, 2383, 2322, 1606, 1530, 1462, 1347, 1306, 1166, 1090, 1001, 887, 860, 765, 738, 715, 679, 639, 616, 570, 540; HRMS (ESI) calcd for C\(_{20}\)H\(_{23}\)N\(_4\)O\(_3\)S [M+NH\(_4\)]\(^+\): 415.1435. Found: 415.1433.

**1f:** (1f was purified by PE/EtOAc = 6:1) yellow solid, 0.85 g, 77% yield, M.P. = 67-68 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.87 (brs, 1H), 7.55 (d, \(J = 7.2\) Hz, 1H), 7.28 (d, \(J = 7.2\) Hz, 1H), 7.15-7.09 (m, 2H), 4.09 (d, \(J = 2.0\) Hz, 2H), 3.47 (t, \(J = 7.6\) Hz, 2H), 3.04 (t,
$J = 8.0 \text{ Hz, } 2\text{H}$, $2.89 \text{ (s, } 3\text{H)}$, $2.41 \text{ (s, } 3\text{H)}$, $2.37 \text{ (t, } J = 2.0 \text{ Hz, } 1\text{H}).^{13}\text{C NMR (100 MHz, CDCl}_3\delta 135.2, 132.1, 128.2, 121.2, 119.4, 117.6, 110.3, 107.5, 77.5, 74.1, 47.0, 37.8, 36.9, 23.9, 11.6. IR (thin film): } \nu_{\text{max}} (\text{cm}^{-1}) 3391, 3273, 2965, 2920, 1459, 1312, 1141, 1088, 1020, 966, 921, 804, 769, 742, 686, 656, 587, 515, 495, 432; \text{HRMS (ESI) calcd for } C_{15}H_{22}N_3O_2S [M+NH}_4\text{]+: 308.1427. \text{ Found: 308.1428.}$

$1g$: ($1g$ was purified by PE/EtOAc = 5:1) white solid, $1.62 \text{ g, 74% yield, M.P. = 134-135 }^\circ\text{C. }^{1}\text{H NMR (400 MHz, CDCl}_3\delta 8.29 \text{ (s, } 1\text{H)}, 8.22 \text{ (br s, } 1\text{H)}, 7.83 \text{ (dd, } J = 8.4, 1.6 \text{ Hz, } 1\text{H)}, 7.70 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H)}, 7.26-7.23 \text{ (m, } 3\text{H)}, 4.38 \text{ (q, } J = 7.2 \text{ Hz, } 2\text{H)}, 4.17 \text{ (d, } J = 2.4 \text{ Hz, } 2\text{H}), 3.40-3.37 \text{ (m, } 2\text{H)}, 3.05-3.01 \text{ (m, } 2\text{H)}, 2.40 \text{ (s, } 3\text{H)}, 2.38 \text{ (s, } 3\text{H)}, 1.40 \text{ (t, } J = 7.2 \text{ Hz, } 3\text{H). }^{13}\text{C NMR (100 MHz, CDCl}_3\delta 167.8, 143.5, 137.9, 135.7, 133.5, 129.5, 128.0, 127.5, 122.7, 121.7, 120.6, 109.8, 109.2, 76.8, 74.1, 60.5, 46.9, 37.2, 23.5, 21.5, 14.5, 11.7. IR (thin film): } \nu_{\text{max}} (\text{cm}^{-1}) 3350, 3268, 2926, 2854, 2384, 2348, 2324, 2259, 2115, 1690, 1620, 1595, 1459, 1367, 1325, 1262, 1220, 1158, 1102, 1011, 899, 812, 767, 742, 709, 656, 582, 540; \text{HRMS (ESI) calcd for } C_{24}H_{30}N_3O_4S [M+NH}_4\text{]+: 456.1952. \text{ Found: 456.1954.}$

$1h$: ($1h$ was purified by PE/EtOAc = 5:1) yellow solid, $1.31 \text{ g, 59% yield, M.P. = 135-138 }^\circ\text{C. }^{1}\text{H NMR (400 MHz, CDCl}_3\delta 7.86 \text{ (brs, } 1\text{H)}, 7.72-7.70 \text{ (m, } 2\text{H)}, 7.59 \text{ (d, } J = 1.6 \text{ Hz, } 1\text{H)}, 7.27 \text{ (s, } 1\text{H)}, 7.25 \text{ (s, } 1\text{H)}, 7.19-7.16 \text{ (m, } 1\text{H)}, 7.13-7.11 \text{ (m, } 1\text{H)}, 4.17 \text{ (d, } J = 2.4 \text{ Hz, } 2\text{H)}, 3.36-3.32 \text{ (m, } 2\text{H)}, 2.97-2.93 \text{ (m, } 2\text{H)}, 2.40 \text{ (s, } 3\text{H)}, 2.39 \text{ (s, } 3\text{H)}, 2.13 \text{ (t, } J = 2.4 \text{ Hz, } 1\text{H). }^{13}\text{C NMR (100 MHz, CDCl}_3\delta 143.6, 135.5, 133.7, 133.5, 130.0, 129.5, 127.5, 123.6, 120.1, 112.4, 111.7, 107.4, 76.7, 74.0, 46.7, 37.0, 23.3, 21.5, 11.5. IR (thin film): } \nu_{\text{max}} (\text{cm}^{-1}) 3337, 3297, 2935, 2916, 2854, 1726, 1597, 1574, 1433, 1334, 1235, 1154, 1092, 1003, 897, 864, 799, 738, 662, 627, 575, 545; \text{HRMS (ESI) calcd for } C_{21}H_{25}BrN_3O_2S [M+NH}_4\text{]+: 462.0845. \text{ Found: 462.0844.}$
**1i:** (1i was purified by PE/EtOAc = 5:1) red solid, 1.16 g, 58% yield, M.P. = 135-138 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (brs, 1H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.42 (s, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.8$ Hz, 1H), 7.04 (dd, $J = 8.4$, 1.6 Hz, 1H), 4.17 (d, $J = 2.4$ Hz, 2H), 3.37-3.33 (m, 2H), 2.97-2.93 (m, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 2.13 (t, $J = 2.4$ Hz, 1H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.5, 135.7, 133.6, 133.5, 129.51, 129.46, 127.5, 125.0, 121.2, 117.2, 111.2, 107.7, 76.8, 73.9, 46.7, 37.0, 23.4, 21.5, 11.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3336, 3298, 2979, 2915, 2863, 1578, 1477, 1456, 1434, 1333, 1154, 1093, 1004, 922, 897, 864, 801, 741, 662, 625, 575, 538; HRMS (ESI) calcd for C$_{21}$H$_{22}$ClN$_2$O$_2$S $[M+H]^+$: 401.1085. Found: 401.1086.

**1j:** (1j was purified by PE/EtOAc = 4:1) yellow solid, 3.74 g, 88% yield, M.P. = 119-120 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (brs, 1H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.16-7.10 (m, 2H), 6.85-6.80 (m, 1H), 4.17 (d, $J = 2.0$ Hz, 2H), 3.37-3.33 (m, 2H), 2.98-2.94 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 2.12 (s, 1H). 

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -124.9 (m). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.7 (d, $J = 232.6$ Hz), 143.6, 135.6, 134.1, 131.6, 129.5, 128.7 (d, $J = 9.5$ Hz), 127.5, 110.80 (d, $J = 9.7$ Hz), 109.0, 108.8, 107.9 (d, $J = 4.4$ Hz), 102.6 (d, $J = 23.4$ Hz), 76.8, 73.8, 46.7, 37.0, 23.5, 21.4, 11.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3428, 3282, 2925, 2323, 1579, 1485, 1445, 1336, 1237, 1155, 1115, 1092, 1000, 898, 851, 819, 797, 741, 719, 661, 603, 582, 536, 512; HRMS (ESI) calcd for C$_{21}$H$_{25}$FN$_3$O$_2$S $[M+NH_4]^+$: 402.1646. Found: 402.1647.

**1k:** (1k was purified by PE/EtOAc = 7:1) brown solid, 1.22 g, 51% yield, M.P. = 69-70 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.72-7.70 (m, 3H), 7.28-7.24 (m, 3H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.04 (dd, $J = 8.4$, 1.6 Hz, 1H), 4.17 (d, $J = 2.4$ Hz, 2H), 3.37-3.33 (m, 2H), 2.97-2.93 (m, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 2.13 (t, $J = 2.4$ Hz, 1H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.5, 135.7, 133.6, 133.5, 129.51, 129.46, 127.5, 125.0, 121.2, 117.2, 111.2, 107.7, 76.8, 73.9, 46.7, 37.0, 23.4, 21.5, 11.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3428, 3282, 2925, 2323, 1579, 1485, 1445, 1336, 1237, 1155, 1115, 1092, 1000, 898, 851, 819, 797, 741, 719, 661, 603, 582, 536, 512; HRMS (ESI) calcd for C$_{21}$H$_{25}$FN$_3$O$_2$S $[M+NH_4]^+$: 402.1646. Found: 402.1647.
Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.20 (d, J = 2.4 Hz, 2H), 3.39-3.35 (m, 2H), 3.00-2.96 (m, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H), 2.08 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.4, 135.8, 133.4, 132.0, 129.4, 128.5, 128.4, 127.6, 122.5, 117.5, 109.9, 107.2, 77.0, 73.6, 46.9, 36.9, 23.5, 21.48, 21.46, 11.5. IR (thin film): $\nu_{max}$ (cm$^{-1}$) 3352, 3303, 2915, 2857, 1594, 1437, 1333, 1155, 1090, 1006, 899, 800, 748, 661, 621, 574, 540; HRMS (ESI) calcd for C$_{22}$H$_{28}$N$_3$O$_2$S [M+NH$_4$]$^+$: 398.1897. Found: 398.1896.

1l: (1l was purified by PE/EtOAc = 6:1) yellow solid, 1.37 g, 85% yield, M.P. = 104-106°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71-7.68 (m, 3H), 7.24 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 6.78-6.75 (m, 1H), 4.17 (d, J = 2.4 Hz, 2H), 3.85 (s, 3H), 3.38-3.34 (m, 2H), 3.01-2.97 (m, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.06 (t, J = 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.8, 143.4, 135.7, 132.8, 130.2, 129.8, 128.7, 127.4, 111.0, 110.6, 107.4, 99.9, 76.9, 73.6, 55.8, 46.7, 36.9, 23.7, 21.4, 11.5. IR (thin film): $\nu_{max}$ (cm$^{-1}$) 3356, 3296, 2926, 2914, 2391, 2115, 1592, 1488, 1445, 1332, 1217, 1154, 1087, 1038, 901, 804, 760, 661, 630, 575, 539; HRMS (ESI) calcd for C$_{22}$H$_{25}$N$_2$O$_3$S [M+H]$^+$: 397.1580. Found: 397.1582.

1m: (1m was purified by PE/EtOAc = 8:1) white solid, 2.80 g, 74% yield, M.P. = 104-106°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (brs, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 7.2 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 4.15 (d, J = 2.4 Hz, 2H), 3.38-3.34 (m, 2H), 3.03-3.00 (m, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 2.08 (t, J = 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.4, 135.7, 132.9, 132.3, 129.8, 129.4, 127.5, 120.4, 120.1, 116.3, 115.7, 109.0, 76.9, 73.7, 46.8, 37.0, 23.8, 21.5, 11.5. IR (thin film): $\nu_{max}$ (cm$^{-1}$) 3387, 3271, 3064, 2964, 2915, 2862, 2117, 1589, 1492, 1456, 1296, 1231, 1199, 1141, 1011, 911, 870, 806, 774, 732, 692, 645, 570, 547, 522, 475; HRMS (ESI) calcd for C$_{21}$H$_{25}$ClN$_3$O$_2$S [M+NH$_4$]$^+$: 418.1351. Found: 418.1352.
1n: (1n was purified by DCM) white solid, 8.62 g, 79% yield, M.P. = 161-163 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (brs, 1H), 7.69-7.67 (m, 3H), 7.59-7.56 (m, 2H), 7.48 (t, $J = 8.0$ Hz, 2H), 7.41-7.38 (m, 2H), 7.24-7.21 (m, 3H), 7.18-7.14 (m, 1H), 4.19 (d, $J = 2.4$ Hz, 2H), 3.55-3.51 (m, 2H), 3.24-3.20 (m, 2H), 2.39 (s, 3H), 2.09 (t, $J = 2.4$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.4, 135.8, 135.7, 135.2, 132.6, 129.4, 129.0, 128.9, 127.90, 127.87, 127.6 122.5, 119.9, 118.9, 110.9, 109.0, 76.9, 73.8, 46.9, 36.7, 24.0, 21.5. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3383, 3293, 3046, 2388, 2338, 2306, 2118, 1593, 1452, 1344, 1152, 997, 925, 889, 820, 776, 741, 697, 661, 604, 579, 536; HRMS (ESI) calcd for C$_{26}$H$_{28}$N$_3$O$_2$S [M+NH$_4$]$^+$: 446.1897. Found: 446.1897.

4b$^3$: (4b was purified by PE/EtOAc = 5:1) white solid, 968.5 mg, 57% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (brs, 1H), 7.86-7.8 (m, 2H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.57-7.53 (m, 1H), 7.49-7.45 (m, 2H), 7.37 (d, $J = 8.4$ Hz, 1H), 7.22-7.18 (m, 1H), 7.14-7.11 (m, 2H), 4.19 (d, $J = 2.4$ Hz, 2H), 3.56-3.52 (m, 2H), 3.11-3.07 (m, 2H), 2.05-2.03 (m, 1H).

4c$^1$: (4c was purified by PE/EtOAc = 3:1) white solid, 1.34 g, 21% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (brs, 1H), 7.70-7.66 (m, 2H), 7.62-7.57 (m, 3H), 7.37 (d, $J = 8.4$ Hz, 1H), 7.23-7.19 (m, 1H), 7.15-7.09 (m, 2H), 4.18 (d, $J = 2.4$ Hz, 2H), 3.54-3.40 (m, 2H), 3.11-3.07 (m, 2H), 2.09 (t, $J = 2.4$ Hz, 1H).

4d$^1$: (4d was purified by PE/EtOAc = 3:1) yellow solid, 2.27 g, 59% yield. $^1$H NMR
(400 MHz, CDCl₃) δ 8.25-8.21 (m, 2H), 8.02 (brs, 1H), 7.96-7.93 (m, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.36-7.33 (m, 1H), 7.22-7.18 (m, 1H), 7.14-7.10 (m, 1H), 7.08 (d, J = 2.4 Hz, 1H), 4.23 (d, J = 2.8 Hz, 2H), 3.59-3.56 (m, 2H), 3.12-3.08 (m, 2H), 2.10 (t, J = 2.4 Hz, 1H).

4e: (4e was purified by PE/EtOAc = 4:1) yellow solid, 1.55 g, 56% yield, M.P. = 85-86 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (brs, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.08 (s, 1H), 4.11 (s, 2H), 3.61 (t, J = 7.2 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H), 2.91 (s, 3H), 2.40 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 127.0, 122.3, 122.0, 119.4, 118.4, 111.7, 111.3, 77.3, 74.3, 46.9, 37.7, 36.4, 24.4. IR (thin film): νmax (cm⁻¹) 3412, 3261, 3119, 3021, 2932, 2899, 2384, 2322, 2112, 1619, 1457, 1315, 1225, 1145, 1096, 1002, 965, 908, 806, 770, 747, 710, 665, 572, 513, 474, 428; HRMS (ESI) calcd for C₁₄H₂₀N₃O₂S [M+NH₄]⁺: 294.1271. Found: 294.1272.

4f: (4f was purified by PE/Acetone = 10:1) yellow solid, 0.79 g, 37% yield, M.P. = 119-120 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (brs, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.4 Hz, 1H), 7.09-7.05 (m, 2H), 6.85 (d, J = 7.2 Hz, 1H), 4.20 (s, 2H), 3.54-3.50 (m, 2H), 3.26-3.22 (m, 2H), 2.72 (s, 3H), 2.01-2.00 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 136.5, 132.7, 130.4, 128.8, 127.5, 125.5, 122.6, 122.0, 121.0, 112.6, 109.2, 76.5, 73.8, 48.2, 36.5, 25.9, 20.1. IR (thin film): νmax (cm⁻¹) 3367, 3288, 3058, 2911, 2121, 1446, 1326, 1155, 1125, 1101, 999, 933, 874, 822, 739, 689, 662, 638, 599, 572; HRMS (ESI) calcd for C₂₀H₂₄N₃O₂S [M+NH₄]⁺: 370.1584. Found: 370.1585.
4g: (4g was purified by PE/Acetone = 10:1) yellow solid, 2.23 g, 66% yield, M.P. = 126-127 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (brs, 1H), 7.87-7.85 (m, 2H), 7.56 (t, \(J = 7.2\) Hz, 1H), 7.47 (t, \(J = 7.6\) Hz, 2H), 7.40 (s, 1H), 7.60 (d, \(J = 8.0\) Hz, 1H), 7.05-7.02 (m, 2H), 4.20 (d, \(J = 2.4\) Hz, 2H), 3.54 (t, \(J = 8.0\) Hz, 2H), 3.06 (t, \(J = 8.4\) Hz, 2H), 2.46 (s, 3H), 2.06-2.05 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.7, 134.4, 132.7, 128.8, 128.6, 127.6, 127.4, 123.7, 122.3, 118.2, 111.5, 110.9, 76.6, 73.7, 46.9, 36.6, 24.2, 21.5. IR (thin film): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3414, 3275, 2925, 2384, 2323, 2114, 1581, 1446, 1339, 1290, 1225, 1160, 1098, 992, 951, 868, 792, 734, 679, 648, 599, 551, 422; HRMS (ESI) calcd for C\(_{20}\)H\(_{24}\)N\(_3\)O\(_2\)S [M+NH\(_4^+\)]: 370.1584. Found: 370.1584.

4h: (4h was purified by PE/EtOAc = 5:1) yellow solid, 2.28 g, 69% yield, M.P. = 89-90 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (brs, 1H), 7.86-7.84 (m, 2H), 7.55 (t, \(J = 7.6\) Hz, 1H), 7.51-7.45 (m, 3H), 7.16 (s, 1H), 7.01 (d, \(J = 1.6\) Hz, 1H), 6.97 (d, \(J = 8.0\) Hz, 1H), 4.19 (d, \(J = 2.4\) Hz, 2H), 3.54 (t, \(J = 9.2\) Hz, 2H), 3.07 (t, \(J = 8.4\) Hz, 2H), 2.47 (s, 3H), 2.05-2.04 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.7, 136.6, 132.6, 131.9, 128.8, 127.6, 125.0, 121.5, 121.2, 118.2, 111.9, 111.1, 76.6, 73.8, 47.0, 36.7, 24.3, 21.6. IR (thin film): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3416, 3262, 3059, 2916, 2854, 2323, 2114, 1628, 1451, 1327, 1229, 1160, 1103, 998, 910, 874, 796, 736, 688, 602, 571, 520, 428; HRMS (ESI) calcd for C\(_{20}\)H\(_{21}\)N\(_2\)O\(_2\)S [M+H\(^+\)]: 353.1318. Found: 353.1319.

4i: (4i was purified by PE/EtOAc = 5:1) yellow solid, 3.54 g, 77% yield, M.P. = 127-128 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (brs, 1H), 7.85 (d, \(J = 7.6\) Hz, 2H), 7.56 (t, \(J = 7.6\) Hz, 1H), 7.49-7.45 (m, 3H), 7.09-7.01 (m, 3H), 4.20 (d, \(J = 2.0\) Hz, 2H), 3.55 (t, \(J =
8.0 Hz, 2H), 3.10 (t, J = 8.0 Hz, 2H), 2.49 (s, 3H), 2.06 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.7, 135.7, 132.6, 128.8, 127.6, 126.7, 122.6, 121.9, 120.4, 119.7, 116.3, 112.6, 76.6, 73.8, 46.9, 36.6, 24.4, 16.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3367, 3271, 3050, 2872, 2338, 2306, 2118, 1584, 1444, 1334, 1229, 1158, 1112, 995, 944, 871, 819, 733, 691, 646, 595, 544; HRMS (ESI) calcd for C$_{20}$H$_{24}$N$_3$O$_2$S [M+NH$_4$]$^+$: 370.1584. Found: 370.1584.

4j: (4j was purified by PE/EtOAc = 6:1) white solid, 1.23 g, 44% yield, M.P. = 96-97 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (brs, 1H), 7.84 (d, J = 6.4 Hz, 2H), 7.52 (d, J = 6.4 Hz, 1H), 7.46-7.44 (m, 2H), 7.24-7.23 (m, 1H), 7.11 (s, 1H), 7.04 (d, J = 3.2 Hz, 2H), 4.16 (s, 2H), 3.59-3.56 (m, 2H), 3.30-3.27 (m, 2H), 1.99 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.7, 137.7, 132.7, 128.8, 127.5, 126.0, 124.2, 123.9, 122.5, 120.3, 112.2, 110.1, 76.7, 73.7, 48.3, 36.7, 25.3. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3361, 3288, 3125, 3065, 2916, 2384, 2323, 2121, 1896, 1613, 1562, 1486, 1446, 1426, 1377, 1330, 1282, 1249, 1229, 1185, 1154, 1102, 996, 929, 870, 834, 774, 732, 686, 646, 603, 551; Anal. calcd for C$_{19}$H$_{17}$ClN$_2$O$_2$S: C, 61.20; H, 4.60; Found: C, 61.02; H, 4.68.

4k: (4k was purified by PE/EtOAc = 5:1) white solid, 1.89 g, 63% yield, M.P. = 118-119 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (brs, 1H), 7.85-7.83 (m, 2H), 7.58-7.54 (m, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 8.8 Hz, 1H), 7.14-7.11 (m, 2H), 4.18 (d, J = 2.4 Hz, 2H), 3.52 (t, J = 7.2 Hz, 2H), 3.02 (t, J = 8.0 Hz, 2H), 2.08 (t, J = 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.5, 134.4, 132.8, 128.9, 128.3, 127.5, 125.1, 123.7, 122.3, 118.0, 112.2, 111.8, 76.4, 74.0, 46.7, 36.6, 23.9. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3397, 3272, 2923, 2845, 2384, 2324, 2113, 1584, 1566, 1448, 1342, 1223, 1160, 1091, 995, 954, 868, 794, 734, 679, 650, 600, 540, 420; HRMS (ESI) calcd for C$_{19}$H$_{21}$ClN$_3$O$_2$S [M+NH$_4$]$^+$: 390.1038. Found: 390.1038.
4l: (4l was purified by PE/EtOAc = 6:1) white solid, 1.57 g, 65% yield, M.P. = 85-86 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (brs, 1H), 7.85-7.82 (m, 2H), 7.58-7.54 (m, 1H), 7.51-7.45 (m, 3H), 7.343-7.339 (m, 1H), 7.09-7.07 (m, 2H), 4.16 (d, $J = 2.4$ Hz, 2H), 3.53-3.50 (m, 2H), 3.07-3.03 (m, 2H), 2.05 (t, $J = 2.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.5, 136.4, 132.8, 128.9, 127.9, 127.5, 125.8, 122.9, 120.1, 119.4, 112.2, 111.1, 76.4, 73.9, 46.8, 36.7, 24.1. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3390, 3266, 3061, 1450, 1411, 1327, 1227, 1159, 1106, 997, 963, 909, 873, 819, 799, 733, 684, 631, 602, 560, 512, 423; HRMS (ESI) calcd for C$_{19}$H$_{21}$ClN$_3$O$_2$S $[\text{M+NH}_4]^+$: 390.1038. Found: 390.1037.

4m: (4m was purified by PE/EtOAc = 10:1) white solid, 1.67 g, 43% yield, M.P. = 116-117 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (brs, 1H), 7.83 (d, $J = 7.6$ Hz, 2H), 7.57-7.51 (m, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.20 (d, $J = 7.6$ Hz, 1H), 7.15 (s, 1H), 7.06 (t, $J = 7.6$ Hz, 1H), 4.17 (d, $J = 2.0$ Hz, 2H), 3.53 (t, $J = 7.6$ Hz, 2H), 3.08 (t, $J = 8.0$ Hz, 2H), 2.05 (t, $J = 2.0$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.7, 132.7, 128.8, 128.7, 127.5, 122.8, 121.5, 120.3, 117.3, 116.7, 113.4, 76.5, 73.8, 46.8, 36.7, 24.4. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3348, 3276, 2322, 1489, 1443, 1331, 1235, 196, 1157, 1107, 999, 940, 869, 827, 774, 732, 688, 656, 611, 590, 546, 454; Anal. calcd for C$_{19}$H$_{17}$ClN$_2$O$_2$: C, 61.02; H, 4.60; Found: C, 60.96; H, 4.47.

4n: (4n was purified by PE/EtOAc = 4:1) white solid, 0.49 g, 21% yield, M.P. = 132-133 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (brs, 1H), 7.85-7.83 (m, 2H), 7.57-7.53 (m, 1H), 7.47 (t, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 1H), 7.09-7.06 (m, 2H), 6.86 (dd, $J = 8.8$,
2.4 Hz, 1H), 4.18 (d, \(J = 2.4\) Hz, 2H), 3.87 (s, 3H), 3.55-3.51 (m, 2H), 3.08-3.04 (m, 2H), 2.03 (t, \(J = 2.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.0, 138.8, 132.7, 131.2, 128.8, 127.6, 127.5, 122.9, 112.4, 111.9, 111.9, 100.3, 76.9, 73.7, 55.8, 46.8, 36.7, 24.4.

IR (thin film): \(v_{\text{max}}\) (cm\(^{-1}\)) 3401, 3259, 2991, 2948, 2909, 2863, 2386, 2348, 2110, 1616, 1583, 1485, 1448, 1339, 1220, 1171, 1128, 1093, 1060, 1027, 991, 925, 896, 831, 807, 745, 715, 691, 602, 554, 502; HRMS (ESI) calcd for C\(_{20}\)H\(_{24}\)N\(_3\)O\(_3\)S [M+NH\(_4\)]\(^+\): 386.1533. Found: 386.1533.

4o: (4o was purified by PE/EtOAc = 4:1) yellow solid, 0.51 g, 23% yield, M.P. = 108-110 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99 (br s, 1H), 7.84 (d, \(J = 7.2\) Hz, 2H), 7.55 (t, \(J = 7.2\) Hz, 1H), 7.50-7.45 (m, 4H), 7.39 (t, \(J = 7.2\) Hz, 2H), 7.32 (t, \(J = 7.2\) Hz, 1H), 7.25 (d, \(J = 8.8\) Hz, 1H), 7.18 (d, \(J = 2.0\) Hz, 1H), 7.05 (d, \(J = 1.6\) Hz, 1H), 6.95 (dd, \(J = 8.4, 2.0\) Hz, 1H), 5.13 (s, 2H), 4.17 (d, \(J = 2.0\) Hz, 2H), 3.53 (t, \(J = 8.0\) Hz, 2H), 3.05 (t, \(J = 8.0\) Hz, 2H), 2.01 (t, \(J = 2.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 153.2, 138.8, 137.6, 132.6, 131.5, 128.8, 128.5, 127.7, 127.5, 127.5, 123.0, 113.1, 111.9, 111.9, 102.0, 73.7, 70.9, 46.9, 36.7, 24.4. IR (thin film): \(v_{\text{max}}\) (cm\(^{-1}\)) 3449, 3276, 2918, 2866, 2396, 2360, 2306, 2119, 1622, 1581, 1450, 1329, 1213, 1159, 1093, 1053, 991, 940, 900, 851, 792, 747, 720, 691, 590, 561, 493, 423; HRMS (ESI) calcd for C\(_{26}\)H\(_{28}\)N\(_3\)O\(_3\)S [M+NH\(_4\)]\(^+\): 462.1846. Found: 462.1848.

4p: (4p was purified by PE/EtOAc = 5:1) white solid, 0.52 g, 86% yield, M.P. = 116-117 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (br s, 1H), 7.84 (d, \(J = 7.6\) Hz, 2H), 7.56 (t, \(J = 7.6\) Hz, 1H), 7.48 (t, \(J = 8.0\) Hz, 2H), 7.29-7.21 (m, 2H), 7.14 (s, 1H), 6.93 (td, \(J = 9.2, 2.4\) Hz, 1H), 4.17 (d, \(J = 2.4\) Hz, 2H), 3.51 (t, \(J = 7.6\) Hz, 2H), 3.03 (t, \(J = 8.0\) Hz, 2H), 2.06 (t, \(J = 2.4\) Hz, 1H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -124.5 (m). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.7 (d, \(J = 233.5\) Hz), 138.6, 132.8, 132.6, 128.9, 127.6, 124.0, 112.3 (d, \(J =
4.4 Hz), 111.84 (d, $J = 9.7$ Hz), 110.5 (d, $J = 26.2$ Hz), 103.5, (d, $J = 23.4$ Hz), 76.5, 73.9, 46.7, 36.7, 24.1. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3374, 3277, 2922, 2879, 2114, 1702, 1624, 1578, 1484, 1448, 1340, 1223, 1161, 1121, 1097, 996, 955, 919, 869, 794, 734, 670, 646, 602, 549, 447, 426; HRMS (ESI) calcd for C$_{19}$H$_{18}$FN$_2$O$_2$S [M+H]$^+$: 357.1068. Found: 357.1068.

$4q$: ($4q$ was purified by PE/EtOAc = 5:1) white solid, 0.40 g, 26% yield, M.P. = 105-106°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (brs, 1H), 7.86-7.83 (m, 2H), 7.71 (d, $J = 1.6$ Hz, 1H), 7.59-7.54 (m, 1H), 7.50-7.47 (m, 2H), 7.27-7.21 (m, 2H), 7.10 (d, $J = 2.0$ Hz, 1H), 4.18 (d, $J = 2.4$ Hz, 2H), 3.51 (t, $J = 8.0$ Hz, 2H), 3.02 (t, $J = 8.0$ Hz, 2H), 2.09 (t, $J = 2.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.5, 134.7, 132.8, 129.0, 128.9, 127.5, 124.8, 123.5, 121.1, 112.7, 112.6, 111.7, 76.4, 74.0, 46.6, 36.6, 23.9. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) 3398, 3272, 3139, 2923, 2895, 2111, 1563, 1448, 1341, 1224, 1159, 1107, 994, 953, 868, 793, 735, 683, 649, 597, 537, 419; HRMS (ESI) calcd for C$_{19}$H$_{21}$BrN$_3$O$_2$S [M+NH$_4$]$^+$: 434.0532. Found: 434.0532.
2.2 General procedure for gold-catalyzed dearomatization of indole derivatives

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added JohnPhosAuCl (5.3 mg, 0.01 mmol, 5 mol %), 1 (0.2 mmol, 1.0 equiv) and DCE (2.0 mL). Then AgOMs (2.0 mg, 0.01 mmol, 5 mol %) was added. The reaction mixture was stirred at 60 °C with oil bath under dark. After the reaction was complete (monitored by TLC or LC-MS), the reaction system was cooled to room temperature and filtered through celite and the mixture was concentrated in vacuo. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 10:1-1:3) to afford the desired product 2. The analytical data of the products are summarized below.

2b: (2b was purified by PE/EtOAc = 2:1) white solid, 68.2 mg, 93% yield, M.P. = 165-166 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 4.86 (s, 1H), 4.43 (s, 1H), 4.25 (AB, $J_{AB} = 14.0$ Hz, 1H), 3.84-3.80 (m, 1H), 3.71 (BA, $J_{BA} = 14.0$ Hz, 1H), 3.17 (td, $J = 12.4$, 3.2 Hz, 1H), 2.47 (s, 3H), 2.19 (s, 3H), 2.13 (td, $J = 12.8$, 4.8 Hz, 1H), 1.42-1.37 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 184.0, 153.5, 143.9, 143.2, 137.9, 133.4, 129.8, 128.1, 127.7, 124.9, 122.0, 120.7, 112.6, 61.1, 49.9, 42.1, 30.7, 21.5, 17.0. IR (thin film): $v_{max}$ (cm$^{-1}$) = 2923, 1578, 1450, 1343, 1155, 1094, 1026, 931, 904, 814, 773, 741, 711, 660, 603, 542, 515; HRMS (ESI) calcd for C$_{21}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 367.1475. Found: 367.1476.

2c: (2c was purified by PE/EtOAc = 1:1) yellowish solid, 64.1 mg, 91% yield, M.P. = 168-169 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90-7.87 (m, 2H), 7.71-7.66 (m, 1H),
7.63-7.59 (m, 2H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.30-7.26 (m, 1H), 7.07-6.99 (m, 2H), 4.88 (s, 1H), 4.45 (d, $J = 1.2$ Hz, 1H), 4.30 (AB, $J_{AB} = 14.0$ Hz, 1H), 3.89-3.84 (m, 1H), 3.75 (BA, $J_{BA} = 14.0$ Hz, 1H), 3.20 (td, $J = 12.4$, 3.2 Hz, 1H), 2.19 (s, 3H), 2.18-2.10 (m, 1H), 1.41 (dt, $J = 13.6$, 3.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 183.9, 153.6, 143.1, 137.9, 136.6, 133.1, 129.3, 128.2, 127.7, 125.0, 122.0, 112.7, 61.1, 50.0, 42.2, 30.7, 17.0. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2924, 2360, 1643, 1582, 1443, 1349, 1249, 1165, 1095, 997, 849, 757, 724, 694, 611, 571; HRMS (ESI) calcd for C$_{20}$H$_{21}$N$_2$O$_2$S [M+H]$^+$: 353.1318. Found: 353.1320.

2d: (2d) was purified by PE/EtOAc = 1:1 white solid, 84.4 mg, 98% yield, M.P. = 154-155 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76-7.71 (m, 4H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 1H), 7.11-7.03 (m, 2H), 4.87 (s, 1H), 4.46 (s, 1H), 4.27 (AB, $J_{AB} = 14.0$ Hz, 1H), 3.85-3.82 (m, 1H), 3.76 (BA, $J_{BA} = 14.0$ Hz, 1H), 3.21 (td, $J = 12.4$, 2.8 Hz, 1H), 2.21 (s, 3H), 1.42 (dt, $J = 13.6$, 3.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 183.7, 153.6, 143.1, 137.7, 135.8, 132.6, 129.1, 128.3, 128.1, 125.1, 121.9, 120.9, 113.0, 61.1, 49.9, 42.2, 30.7, 17.0. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3094, 3072, 2954, 2924, 2845, 2386, 1645, 1572, 1466, 1352, 1226, 1168, 1093, 1064, 1003, 917, 895, 852, 826, 761, 735, 632, 613, 587, 521, 478, 444, 417; HRMS (ESI) calcd for C$_{20}$H$_{20}$BrN$_2$O$_2$S [M+H]$^+$: 431.0423. Found: 431.0426.

2e: (2e) was purified by PE/EtOAc = 1:1 yellowish solid, 73.4 mg, 92% yield, M.P. = 217-218 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J = 8.8$ Hz, 2H), 8.06 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 4.91 (s, 1H), 4.49 (s, 1H), 4.33 (AB, $J_{AB} = 14.4$ Hz, 1H), 3.92-3.89 (m, 1H), 3.84 (d, $J = 14.0$ Hz, 1H), 3.29 (td, $J = 12.0$, 2.8 Hz, 1H), 2.22 (s, 3H), 2.16 (td, $J = 13.2$, 4.8 Hz, 1H), 1.47 (dt, $J = 13.6$, 3.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 183.4,
153.6, 150.2, 143.0, 142.9, 137.4, 128.8, 128.4, 125.1, 124.5, 121.8, 120.9, 113.2, 61.0, 49.9, 42.2, 30.8, 17.0. IR (thin film): ν_{max} (cm\(^{-1}\)) = 3070, 2951, 2922, 2856, 1582, 1529, 1464, 1350, 1312, 1167, 1100, 999, 927, 898, 759, 684, 616, 593, 573, 512, 465; HRMS (ESI) calcd for C\(_{20}\)H\(_{20}\)N\(_3\)O\(_4\)S \([M+H]^+\): 398.1169. Found: 398.1172.

2f: (2f was purified by PE/EtOAc = 1:3) yellowish solid, 49.6 mg, 89% yield, M.P. = 146-147 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.56 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H) 7.34 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 4.90 (s, 1H), 4.52 (s, 1H), 4.29 (AB, J\(_{AB}\) = 14.0 Hz, 1H), 4.02 (BA, J\(_{BA}\) = 14.0 Hz, 1H), 3.90-3.87 (m, 1H), 3.49 (td, J = 12.4, 2.8 Hz, 1H), 2.95 (s, 3H), 2.34 (s, 3H), 2.25 (td, J = 13.2, 4.4 Hz, 1H), 1.55-1.51 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 183.8, 153.7, 143.2, 138.0, 128.4, 125.2, 122.1, 121.0, 112.8, 61.3, 49.7, 42.0, 36.4, 31.3, 17.2. IR (thin film): ν_{max} (cm\(^{-1}\)) = 2920, 2323, 1643, 1579, 1452, 1324, 1152, 1094, 928, 779, 742, 658, 602, 565, 543, 517; HRMS (ESI) calcd for C\(_{15}\)H\(_{19}\)N\(_2\)O\(_2\)S \([M+H]^+\): 291.1162. Found: 291.1165.

2g: (2g was purified by PE/EtOAc = 1:1) yellowish solid, 80.6 mg, 94% yield, M.P. = 154-155 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.00 (d, J = 8.0 Hz, 1H), 7.78-7.74 (m, 3H), 7.52 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 4.88 (s, 1H), 4.42 (s, 1H), 4.31-4.25 (m, 3H), 3.88-3.85 (m, 1H), 3.74 (BA, J\(_{BA}\) = 14.0 Hz, 1H), 3.19 (td, J = 12.4, 2.4 Hz, 1H), 2.46 (s, 3H), 2.23 (s, 3H), 2.15 (td, J = 13.2, 4.8 Hz, 1H), 1.44-1.41 (m, 1H), 1.30 (t, J = 7.2 Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 187.6, 166.0, 157.4, 144.1, 143.3, 137.5, 133.4, 130.4, 129.9, 127.7, 127.1, 123.0, 120.4, 113.1, 61.3, 60.9, 50.1, 42.3, 30.7, 21.5, 17.4, 14.2. IR (thin film): ν_{max} (cm\(^{-1}\)) = 2984, 2856, 2832, 1713, 1578, 1461, 1350, 1291, 1243, 1163, 1100, 1021, 918, 855, 818, 785, 754, 709, 659, 606, 579, 545, 517; HRMS (ESI) calcd for C\(_{24}\)H\(_{30}\)N\(_3\)O\(_4\)S \([M+NH_4]^+\): 456.1952. Found: 456.1953.
2h: (2h was purified by PE/EtOAc = 1:1) white solid, 87.7 mg, 98% yield, M.P. = 176-177 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.0 Hz, 2H), 7.45-7.37 (m, 4H), 7.03 (s, 1H), 4.93 (s, 1H), 4.48 (s, 1H), 4.27 (AB, Jₓᵧ = 14.4 Hz, 1H), 3.84 (d, J = 12.0 Hz, 1H), 3.67 (BA, Jₓᵧ = 14.4 Hz, 1H), 3.11 (td, J = 12.4 Hz, 3.2 Hz, 1H), 2.51 (s, 3H), 2.23 (s, 3H), 2.16 (td, J = 12.4 Hz, 4.8 Hz, 1H), 1.45 (d, J = 13.2 Hz, 3.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.5, 152.6, 144.9, 144.2, 137.3, 132.8, 129.9, 127.8, 125.5, 122.0, 118.5, 113.3, 61.5, 49.8, 42.0, 30.5, 21.6, 17.2. IR (thin film): νₓᵧ (cm⁻¹) = 2922, 2360, 1578, 1445, 1348, 1163, 1094, 903, 878, 830, 762, 709, 659, 631, 607, 581, 547, 444; HRMS (ESI) calcd for C₂₁H₂₂BrN₂O₂S [M+H]⁺: 445.0580. Found: 445.0581.

2i: (2i was purified by PE/EtOAc = 1:1) yellowish solid, 70.0 mg, 88% yield, M.P. = 177-178 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.0 Hz, 2H), 7.42-7.40 (m, 3H), 7.24-7.22 (m, 1H), 6.87 (s, 1H), 4.90 (s, 1H), 4.44 (s, 1H), 4.24 (AB, Jₓᵧ = 14.0 Hz, 1H), 3.83-3.79 (m, 1H), 3.67 (BA, Jₓᵧ = 14.4 Hz, 1H), 3.11 (td, J = 12.0 Hz, 2.8 Hz, 1H), 2.47 (s, 3H), 2.21 (s, 3H), 2.13 (td, J = 13.2 Hz, 4.4 Hz, 1H), 1.44-1.40 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.5, 152.2, 144.6, 144.2, 137.3, 133.0, 130.6, 129.9, 128.2, 127.8, 122.7, 121.5, 113.3, 61.5, 49.8, 42.0, 30.5, 21.6, 17.3. IR (thin film): νₓᵧ (cm⁻¹) = 2922, 1578, 1445, 1348, 1163, 1090, 904, 832, 764, 723, 658, 631, 608, 586, 547, 521, 446; HRMS (ESI) calcd for C₂₁H₂₂ClN₂O₂S [M+H]⁺: 401.1085. Found: 401.1089.

2j: (2j was purified by PE/EtOAc = 1:1) yellowish solid, 71.0 mg, 92% yield, M.P. = 177-178 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 2H), 7.44-7.39 (m, 3H), 6.98-6.93 (m, 1H), 6.68-6.66 (m, 1H), 4.91 (s, 1H), 4.46 (s, 1H), 4.25 (AB, Jₓᵧ = 14.4
Hz, 1H), 3.83-3.80 (m, 1H), 3.66 (BA, J_{BA} = 14.4 Hz, 1H), 3.11 (td, J = 12.4, 2.8 Hz, 1H), 2.48 (s, 3H), 2.20 (s, 3H), 2.17-2.10 (m, 1H), 1.46-1.42 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -116.6 (m). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 183.8 (d, $J$ = 3.6 Hz), 160.3 (d, $J$ = 243.2 Hz), 149.7, 144.7 (d, $J$ = 8.5 Hz), 144.2, 137.5, 133.2, 129.9, 127.7, 121.3 (d, $J$ = 8.9 Hz), 114.6 (d, $J$ = 23.3 Hz), 113.3, 110.3 (d, $J$ = 25.2 Hz), 61.5, 49.8, 42.0, 30.6, 21.5, 17.1. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 1592, 1460, 1343, 1248, 1189, 1156, 1092, 1029, 925, 816, 791, 738, 710, 661, 590, 545, 518; HRMS (ESI) calcd for C$_{21}$H$_{22}$FN$_2$O$_2$S [M+H]$^+$: 385.1381. Found: 385.1384.

2k: (2k was purified by PE/EtOAc = 1:1) yellowish solid, 72.1 mg, 95% yield, M.P. = 192-193 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.43 (d, $J$ = 8.4 Hz, 2H), 7.39 (d, $J$ = 8.0 Hz, 1H) 7.08 (d, $J$ = 7.6 Hz, 1H), 6.76 (s, 1H), 4.89 (s, 1H), 4.47 (s, 1H), 4.26 (AB, $J_{AB}$ = 14.0 Hz, 1H), 3.82 (dt, $J$ = 12.4, 3.6 Hz, 1H), 3.75 (BA, $J_{BA}$ = 14.0 Hz, 1H), 3.21 (td, $J$ = 12.4, 3.2 Hz, 1H), 2.50 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H), 2.14 (td, $J$ = 13.2, 4.8 Hz, 1H), 1.42 (dt, $J$ = 13.6, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 182.8, 151.3, 143.9, 143.1, 138.1, 134.5, 133.2, 129.8, 128.6, 127.9, 123.1, 120.3, 112.5, 60.9, 49.8, 42.0, 30.6, 21.5, 21.3, 17.0. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2949, 2920, 2852, 2364, 2335, 1580, 1462, 1344, 1155, 1093, 1027, 914, 815, 739, 711, 662, 607, 583, 545, 518; HRMS (ESI) calcd for C$_{22}$H$_{25}$N$_2$O$_2$S [M+H]$^+$: 381.1631. Found: 381.1635.

2l: (2l was purified by PE/EtOAc = 1:1) yellowish solid, 66.8 mg, 84% yield, M.P. = 179-180 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J$ = 8.4 Hz, 2H), 7.40-7.37 (m, 3H), 6.77 (dd, $J$ = 8.8, 2.4 Hz, 1H), 6.57 (d, $J$ = 2.4 Hz, 1H), 4.87 (s, 1H), 4.45 (s, 1H), 4.22 (AB, $J_{AB}$ = 14.0 Hz, 1H), 3.78 (dt, $J$ = 12.4, 3.6 Hz, 1H), 3.68 (BA, $J_{BA}$ = 14.0 Hz, 1H), 3.63 (s, 3H), 3.14 (td, $J$ = 12.0, 2.8 Hz, 1H), 2.45 (s, 3H), 2.16 (s, 3H), 2.12 (td, $J$ = 13.2, 4.8 Hz, 1H), 1.42 (dt, $J$ = 13.2, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 181.6, 157.2,
147.2, 144.5, 144.0, 137.9, 133.1, 129.8, 127.8, 120.8, 112.9, 112.1, 109.4, 61.1, 55.4, 49.8, 41.9, 30.7, 21.5, 17.0. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2948, 2919, 2829, 2384, 2321, 1648, 1586, 1472, 1351, 1287, 1258, 1166, 1096, 1043, 939, 914, 888, 830, 753, 658, 598, 566, 545, 522, 445.

HRMS (ESI) calcd for C$_{22}$H$_{25}$N$_2$O$_3$S [M+H]$^+$: 397.1580. Found: 397.1583.

$2m$: ($2m$ was purified by PE/EtOAc = 2:1) yellowish solid, 78.9 mg, 99% yield, M.P. = 188-189 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 8.0 Hz, 2H), 7.39 (d, $J$ = 7.6 Hz, 2H), 7.28-7.25 (m, 1H), 6.98-6.94 (m, 2H), 4.90 (s, 1H), 4.46 (s, 1H), 4.23 (AB, $J_{AB}$ = 14.4 Hz, 1H), 3.80 (dt, $J$ = 7.6, 3.6 Hz, 1H), 3.72 (BA, $J_{BA}$ = 14.0 Hz, 1H), 3.17 (td, $J$ = 12.0, 2.8 Hz, 1H), 2.47 (s, 3H), 2.24 (s, 3H), 2.13 (td, $J$ = 12.8, 4.8 Hz, 1H), 1.46-1.42 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 185.6, 150.3, 145.0, 137.3, 133.4, 129.9, 128.6, 127.7, 126.1, 125.6, 120.4, 113.4, 62.4, 49.8, 42.0, 30.6, 21.5, 17.3. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2920, 1575, 1423, 1346, 1214, 1160, 1094, 1058, 926, 814, 752, 708, 662, 630, 603, 571, 545, 514; HRMS (ESI) calcd for C$_{21}$H$_{22}$ClN$_2$O$_2$S [M+H]$^+$: 401.1085. Found: 401.1088.

$2n$: ($2n$ was purified by PE/EtOAc = 10:1) white solid, 85.1 mg, 99% yield, M.P. = 156-157 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17-8.15 (m, 2H), 7.80 (d, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.48-7.43 (m, 5H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.17 (d, $J$ = 7.2 Hz, 1H), 7.06 (t, $J$ = 7.2 Hz, 1H), 4.90 (s, 1H), 4.56 (s, 1H), 4.47 (AB, $J_{AB}$ = 14.0 Hz, 1H), 3.96-3.92 (m, 1H), 3.71 (BA, $J_{BA}$ = 13.6 Hz, 1H), 3.09 (td, $J$ = 12.4, 2.8 Hz, 1H), 2.67 (td, $J$ = 13.2, 5.2 Hz, 1H), 2.52 (s, 3H), 1.45-1.41 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 179.7, 152.9, 145.4, 144.0, 138.7, 132.9, 131.1, 130.9, 129.9, 129.7, 128.33, 128.29, 127.8, 125.3, 122.0, 121.5, 113.8, 60.2, 50.3, 42.6, 32.2, 21.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$)
The procedure for a gram-scale synthesis of product 2n

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added JohnPhosAuCl (79.5 mg, 0.15 mmol, 5 mol %), 1n (1286 mg, 3.0 mmol, 1.0 equiv) and DCE (30.0 mL). Then AgOMs (30.0 mg, 0.15 mmol, 5 mol %) was added. The reaction mixture was stirred at 60 °C with oil bath under dark. After the reaction was complete (monitored by TLC), the reaction system was cooled to room temperature and filtered through celite and the mixture was concentrated in vacuo. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford the desired product 2n (1.28 g, 99% yield).
2.3 General procedure for gold-catalyzed cascade dearomatization of indole derivatives

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added JohnPhosAuCl (5.3 mg, 0.01 mmol, 5 mol %), 4 (0.2 mmol, 1.0 equiv), Hantzsch ester (0.24 mmol, 1.2 equiv) and DCM (2.0 mL). Then AgOMs (2.0 mg, 0.01 mmol, 5 mol %) was added. The reaction mixture was stirred at room temperature under dark. After the reaction was complete (monitored by TLC or LC-MS), the reaction system was filtered through celite and the mixture was concentrated in vacuo. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 10:1-1:1-EA) to afford the desired product 3. The analytical data of the products are summarized below.

3a: (3a was purified by PE/EtOAc = 2:1) white solid, 51.2 mg, 72% yield, M.P. = 183-184 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.07 (td, $J = 7.6$, 1.2 Hz, 1H), 6.94 (d, $J = 6.8$ Hz, 1H), 6.76 (td, $J = 7.6$, 0.8 Hz, 1H), 6.66 (d, $J = 7.6$ Hz, 1H), 5.02 (s, 1H), 4.56 (s, 1H), 4.26 (dd, $J = 12.8$, 1.6 Hz, 1H), 3.86-3.80 (m, 1H), 3.65 (brs, 1H), 3.36 (AB, $J_{AB} = 13.2$ Hz, 1H), 3.31 (BA, $J_{BA} = 13.2$ Hz, 1H), 3.15 (d, $J = 12.8$ Hz, 1H), 2.58 (td, $J = 12.4$, 2.8 Hz, 1H), 2.46 (s, 3H), 2.07 (td, $J = 13.2$, 4.8 Hz, 1H), 1.83 (dt, $J = 13.6$, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.8, 143.8, 143.7, 133.0, 132.2, 129.7, 128.3, 127.8, 124.5, 118.9, 113.6, 110.2, 57.1, 50.7, 50.2, 43.6, 35.8, 21.5. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3407, 2919, 2849, 2123, 2081, 1925, 1726, 1601, 1489, 1462, 1336, 1253, 1162, 1093, 1019, 957, 910, 815, 745, 662, 617, 567, 544, 459; HRMS (ESI) calcd for C$_{20}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 355.1475. Found: 355.1479.
3b: (3b was purified by PE/EtOAc = 2:1) white solid, 53.4 mg, 79% yield, M.P. = 127-128 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J = 7.2$ Hz, 2H), 7.64 (t, $J = 7.2$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 2H), 7.06 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 7.2$ Hz, 1H), 6.73 (t, $J = 7.2$ Hz, 1H), 6.64 (d, $J = 8.0$ Hz, 1H), 5.00 (s, 1H), 4.55 (s, 1H), 4.27 (AB, $J_{AB} = 13.2$ Hz, 1H), 3.85-3.79 (m, 2H), 3.33 (AB, $J_{AB} = 8.8$ Hz, 1H), 3.28 (BA, $J_{BA} = 9.2$ Hz, 1H), 3.18 (BA, $J_{BA} = 13.2$ Hz, 1H), 2.61 (td, $J = 12.4$, 2.4 Hz, 1H), 2.03 (td, $J = 12.4$, 4.4 Hz, 1H), 1.82-1.79 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.8, 143.6, 135.9, 132.8, 131.9, 128.9, 128.1, 127.5, 124.2, 118.5, 113.4, 110.0, 56.9, 50.6, 49.9, 43.5, 35.5. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3394, 2928, 2848, 1604, 1461, 1349, 1314, 1166, 1091, 1019, 907, 754, 690, 626, 571, 458; HRMS (ESI) calcd for C$_{19}$H$_{21}$N$_2$O$_2$S [M+H]$^+$: 341.1318. Found: 341.1320.

3c: (3c was purified by PE/EtOAc = 6:1) white solid, 63.0 mg, 75% yield, M.P. = 183-184 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72-7.67 (m, 4H), 7.08 (td, $J = 7.6$, 1.2 Hz, 1H), 6.93 (d, $J = 6.8$ Hz, 1H), 6.77 (td, $J = 7.2$, 0.8 Hz, 1H), 6.66 (d, $J = 8.0$ Hz, 1H), 5.03 (s, 1H), 4.58 (s, 1H), 4.26 (dd, $J = 13.2$, 1.6 Hz, 1H), 3.85-3.82 (m, 1H), 3.73 (brs, 1H), 3.38 (AB, $J_{AB} = 9.2$ Hz, 1H), 3.34 (BA, $J_{BA} = 9.2$ Hz, 1H), 3.21 (d, $J = 12.8$ Hz, 1H), 2.64 (td, $J = 12.4$, 2.8 Hz, 1H), 2.06 (td, $J = 13.2$, 4.4 Hz, 1H), 1.84 (dt, $J = 14.0$, 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.8, 143.5, 135.4, 132.4, 132.0, 129.2, 128.4, 127.9, 124.5, 118.9, 113.9, 110.2, 57.1, 50.7, 50.2, 43.6, 35.7. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3407, 2848, 2323, 1601, 1489, 1463, 1335, 1252, 1226, 1163, 1094, 1020, 957, 910, 816, 746, 663, 617, 567, 545, 460; HRMS (ESI) calcd for C$_{19}$H$_{20}$BrN$_2$O$_2$S [M+H]$^+$: 419.0423. Found: 419.0424.
3d: (3d was purified by PE/EtOAc = 2:1) yellow solid, 50.0 mg, 62% yield, M.P. = 127-128 °C. $^1$H NMR (400 MHz, $d_6$-DMSO) δ 8.46 (d, $J = 8.8$ Hz, 2H), 8.08 (d, $J = 8.8$ Hz, 2H), 6.95 (t, $J = 7.2$ Hz, 1H), 6.78 (d, $J = 7.2$ Hz, 1H), 6.54 (t, $J = 7.2$ Hz, 1H), 6.50 (d, $J = 7.6$ Hz, 1H), 5.52 (s, 1H), 5.01 (s, 1H), 4.37 (s, 1H), 4.21 (d, $J = 13.2$ Hz, 1H), 3.76 (d, $J = 12.4$ Hz, 1H), 3.33-3.19 (m, 3H), 2.74 (t, $J = 12.4$ Hz, 1H), 1.89-1.81 (m, 1H), 1.74 (d, $J = 13.6$ Hz, 1H). $^{13}$C NMR (100 MHz, $d_6$-DMSO) δ 152.5, 150.6, 145.0, 142.4, 132.2, 129.8, 128.6, 125.3, 124.6, 117.4, 113.3, 109.7, 57.1, 50.7, 50.3, 44.00, 36.0. IR (thin film): $\nu_{max}$(cm$^{-1}$) = 3401, 2959, 2920, 2852, 1727, 1603, 1531, 1463, 1348, 1311, 1258, 1166, 1091, 1016, 957, 913, 856, 801, 768, 740, 683, 629, 590, 561, 459; HRMS (ESI) calcd for C$_{19}$H$_{20}$N$_3$O$_3$S [M+H]$^+$: 386.1169. Found: 386.1169.

3e: (3e was purified by PE/EtOAc = 1:1-EA) white solid, 41.2 mg, 74% yield, M.P. = 181-182 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.11 (td, $J = 7.6$, 1.2 Hz, 1H), 7.06 (d, $J = 6.8$ Hz, 1H), 6.80 (td, $J = 7.6$, 0.8 Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 5.06 (s, 1H), 4.64 (s, 1H), 4.26 (dd, $J = 14.0$, 2.0 Hz, 1H), 3.92-3.86 (m, 1H), 3.75 (brs, 1H), 3.61 (d, $J = 13.2$ Hz, 1H), 3.57 (s, 2H), 3.05 (td, $J = 12.4$, 2.8 Hz, 1H), 2.88 (s, 3H), 2.15 (td, $J = 13.2$, 4.4 Hz, 1H), 1.93 (dt, $J = 14.0$, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.9, 144.0, 132.1, 128.5, 124.5, 119.0, 113.6, 110.3, 57.2, 50.4, 50.3, 43.4, 36.5, 36.1. IR (thin film): $\nu_{max}$(cm$^{-1}$) = 3377, 2921, 2853, 1602, 1485, 1461, 1313, 1148, 1020, 965, 941, 904, 755, 658, 617, 544, 507, 464; HRMS (ESI) calcd for C$_{14}$H$_{19}$N$_2$O$_2$S [M+H]$^+$: 279.1162. Found: 279.1165.
**3f**: (3f was purified by PE/EtOAc = 2:1) white solid, 49.3 mg, 70% yield, M.P. = 152-153 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84-7.81 (m, 2H), 7.65-7.61 (m, 1H), 7.59-7.54 (m, 2H), 6.98 (t, $J = 7.6$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.49 (d, $J = 7.6$ Hz, 1H), 5.05 (s, 1H), 4.52 (s, 1H), 4.34 (dd, $J = 13.2$, 2.0 Hz, 1H), 3.91-3.86 (m, 1H), 3.65 (brs, 1H), 3.38 (AB, $J_{AB} = 8.8$ Hz, 1H), 3.28 (BA, $J_{BA} = 9.2$ Hz, 1H), 3.18 (d, $J = 13.6$ Hz, 1H), 2.56 (td, $J = 12.8$, 2.8 Hz, 1H), 2.36 (td, $J = 13.2$, 4.4 Hz, 1H), 2.11 (s, 3H), 1.80 (dt, $J = 13.6$, 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.2, 142.2, 136.3, 135.6, 129.1, 128.4, 127.7, 122.0, 113.5, 107.8, 57.6, 51.2, 50.5, 43.5, 33.8, 19.4.

IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3319, 2972, 2924, 2881, 1588, 1379, 1088, 1046, 880, 768, 681, 616, 571; HRMS (ESI) calcd for C$_{20}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 355.1475. Found: 355.1477.

**3g**: (3g was purified by PE/EtOAc = 2:1) white solid, 49.1 mg, 69% yield, M.P. = 140-141 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84-7.82 (m, 2H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 2H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.73 (s, 1H), 6.58 (d, $J = 8.0$ Hz, 1H), 5.02 (s, 1H), 4.57 (s, 1H), 4.27 (dd, $J = 13.2$, 1.6 Hz, 1H), 3.87-3.82 (m, 1H), 3.48 (brs, 1H), 3.33 (AB, $J_{AB} = 9.2$ Hz, 1H), 3.30 (BA, $J_{BA} = 8.8$ Hz, 1H) 3.20 (d, $J = 12.8$ Hz, 1H), 2.62 (td, $J = 12.4$, 2.8 Hz, 1H), 2.25 (s, 3H), 2.06 (td, $J = 13.2$, 4.4 Hz, 1H), 1.81 (dt, $J = 13.6$, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.4, 143.7, 136.2, 132.8, 123.6, 129.1, 128.7, 128.3, 127.7, 125.1, 113.6, 110.3, 57.4, 50.7, 50.2, 43.7, 35.6, 20.8. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3395, 2920, 2849, 1616, 1498, 1446, 1335, 1259, 1168, 1090, 963, 910, 815, 773, 725, 693, 626, 579, 558, 458; HRMS (ESI) calcd for C$_{20}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 355.1475. Found: 355.1475.
3h: (3h was purified by PE/EtOAc = 2:1) white solid, 51.9 mg, 73% yield, M.P. = 177-178 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84-7.81 (m, 2H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 2H), 6.80 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.49 (s, 1H), 5.02 (s, 1H), 4.59 (s, 1H), 4.27 (dd, J = 13.2, 2.0 Hz, 1H), 3.87-3.81 (m, 1H), 3.63 (brs, 1H), 3.35 (AB, J$_{AB}$ = 9.2 Hz, 1H), 3.31 (BA, J$_{BA}$ = 8.8 Hz, 1H), 3.20 (d, J = 13.6 Hz, 1H), 2.63 (td, J = 12.4, 2.8 Hz, 1H), 2.26 (s, 3H), 2.04 (td, J = 13.6, 4.8 Hz, 1H), 1.81 (dt, J = 13.6, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.0, 143.8, 138.4, 136.3, 132.8, 129.4, 129.1, 127.7, 124.2, 119.7, 113.5, 111.0, 57.3, 50.7, 49.9, 43.7, 35.8, 21.4. IR (thin film): $\nu_{\max}$ (cm$^{-1}$) = 3397, 3372, 2917, 2842, 1610, 1444, 1331, 1306, 1258, 1228, 1163, 1090, 1021, 959, 908, 853, 800, 768, 728, 684, 616, 567, 451; HRMS (ESI) calcd for C$_{20}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 355.1475. Found: 355.1478.

3i: (3i was purified by PE/EtOAc = 2:1) white solid, 50.2 mg, 71% yield, M.P. = 199-200 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85-7.82 (m, 2H), 7.67-7.63 (m, 1H), 7.59-7.55 (m, 2H), 6.93 (d, J = 6.8 Hz, 1H), 6.79 (d, J = 6.8 Hz, 1H), 6.71 (t, J = 7.2 Hz, 1H), 5.02 (s, 1H), 4.56 (s, 1H), 4.28 (dd, J = 13.2, 1.6 Hz, 1H), 3.88-3.83 (m, 1H), 3.54 (brs, 1H), 3.38 (AB, J$_{AB}$ = 9.2 Hz, 1H), 3.35 (BA, J$_{BA}$ = 9.2 Hz, 1H), 3.22 (d, J = 12.8 Hz, 1H), 2.65 (td, J = 12.4, 2.8 Hz, 1H), 2.12 (s, 3H), 2.05 (td, J = 13.2, 4.4 Hz, 1H), 1.82 (dt, J = 13.6, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.3, 143.8, 136.4, 132.8, 131.5, 129.2, 129.1, 127.7, 122.0, 119.6, 119.1, 113.7, 57.1, 50.7, 50.5, 43.6, 35.9, 16.6. IR (thin film): $\nu_{\max}$ (cm$^{-1}$) = 3377, 3092, 3061, 2960, 2926, 2845, 1649, 1601, 1448, 1330, 1226, 1160, 1095, 1025, 61, 914, 823, 772, 745, 693, 627, 575; HRMS (ESI) calcd for C$_{20}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 355.1475. Found: 355.1477.
**3j:** (3j) was purified by PE/EtOAc = 4:1 white solid, 48.8 mg, 65% yield, M.P. = 177-178 °C. $^1$H NMR (400 MHz, $d_6$-DMSO) $\delta$ 7.80-7.78 (m, 2H), 7.72-7.68 (m, 1H), 7.64-7.60 (m, 2H), 6.94 (t, $J$ = 8.0 Hz, 1H), 6.46 (d, $J$ = 8.0 Hz, 1H), 6.41 (d, $J$ = 8.0 Hz, 1H), 5.91 (s, 1H), 5.05 (s, 1H), 4.27 (s, 1H), 4.24 (dd, $J$ = 13.6, 1.6 Hz, 1H), 3.75 (dd, $J$ = 10.4, 2.0 Hz, 1H), 3.37-3.34 (m, 1H), 3.26-3.21 (m, 2H), 2.63-2.56 (m, 1H), 2.49-2.41 (m, 2H), 1.67-1.63 (m, 1H). $^{13}$C NMR (100 MHz, $d_6$-DMSO) $\delta$ 154.8, 142.0, 137.0, 133.6, 131.0, 130.5, 130.0, 128.0, 127.5, 118.2, 113.0, 108.0, 57.3, 51.9, 50.2, 43.3, 33.4. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3363, 2921, 2854, 2321, 1599, 1445, 1324, 1263, 1162, 1088, 1041, 992, 952, 916, 794, 754, 727, 691, 632, 611, 578, 455; HRMS (ESI) calcd for C$_{19}$H$_{20}$ClN$_2$O$_2$S [M+H]$^+$: 375.0929. Found: 375.0923.

**3k:** (3k) was purified by PE/EtOAc = 2:1 white solid, 58.6 mg, 78% yield, M.P. = 150-151 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83-7.80 (m, 2H), 7.67-7.63 (m, 1H), 7.59-7.55 (m, 2H), 7.00 (dd, $J$ = 8.4, 2.4 Hz, 1H), 6.81 (d, $J$ = 2.0 Hz, 1H), 6.55 (d, $J$ = 8.4 Hz, 1H), 5.04 (s, 1H), 4.57 (s, 1H), 4.27 (dd, $J$ = 13.2, 1.6 Hz, 1H), 3.87-3.81 (m, 1H), 3.73 (brs, 1H), 3.38 (AB, $J_{AB}$ = 9.2 Hz, 1H), 3.32 (BA, $J_{BA}$ = 9.2 Hz, 1H), 3.18 (d, $J$ = 13.2 Hz, 1H), 2.62 (td, $J$ = 12.4, 2.8 Hz, 1H), 1.97 (td, $J$ = 13.2, 4.4 Hz, 1H), 1.80 (dt, $J$ = 13.6, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 143.2, 136.3, 134.0, 133.0, 129.1, 128.2, 127.7, 124.6, 123.3, 113.9, 110.9, 57.5, 50.6, 50.3, 43.4, 35.6. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3383, 2965, 2923, 2863, 2603, 1487, 1443, 1337, 1259, 1162, 1087, 913, 809, 763, 727, 694, 629, 576, 462; HRMS (ESI) calcd for C$_{19}$H$_{20}$ClN$_2$O$_2$S [M+H]$^+$: 375.0929. Found: 375.0930.
3l: (3l was purified by PE/EtOAc = 4:1) white solid, 51.4 mg, 69% yield, M.P. = 182-183 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J = 7.6$ Hz, 2H), 7.64 (t, $J = 6.8$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 2H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 6.60 (s, 1H), 5.03 (s, 1H), 4.57 (s, 1H), 4.27 (d, $J = 13.2$ Hz, 1H), 3.84 (d, $J = 12.4$ Hz, 1H), 6.60 (s, 1H), 5.03 (s, 1H), 4.57 (s, 1H), 4.27 (d, $J = 13.2$ Hz, 1H), 3.84 (d, $J = 12.4$ Hz, 1H), 3.59 (brs, 1H), 3.39 (AB, $J_{AB} = 9.2$ Hz, 1H), 3.32 (BA, $J_{BA} = 8.8$ Hz, 1H), 3.15 (d, $J = 13.2$ Hz, 1H), 2.60 (td, $J = 12.4$, 2.0 Hz, 1H), 1.99 (td, $J = 13.2$, 4.0 Hz, 1H), 1.80 (d, $J = 13.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.0, 143.5, 136.2, 133.9, 132.9, 130.6, 129.1, 127.7, 125.3, 118.5, 113.8, 110.0, 57.4, 50.6, 49.7, 43.5, 35.8. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3401, 2981, 2916, 2842, 1605, 1489, 1444, 1333, 1309, 1254, 1228, 1164, 1091, 1068, 1020, 959, 910, 838, 777, 729, 683, 629, 605, 572, 452; HRMS (ESI) calcd for C$_{19}$H$_{20}$ClN$_2$O$_2$S [M+H]$^+$: 375.0929. Found: 375.0942.

3m: (3m was purified by PE/EtOAc = 10:1) white solid, 46.2 mg, 62% yield, M.P. = 198-199 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J = 7.2$ Hz, 2H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.58 (t, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 7.2$ Hz, 1H), 6.68 (t, $J = 7.6$ Hz, 1H), 5.05 (s, 1H), 4.59 (s, 1H), 4.29 (d, $J = 13.2$ Hz, 1H), 3.91 (s, 1H), 3.86 (d, $J = 13.2$ Hz, 1H), 3.44 (AB, $J_{AB} = 9.2$ Hz, 1H), 3.38 (BA, $J_{BA} = 9.2$ Hz, 1H), 3.17 (d, $J = 13.2$ Hz, 1H), 2.62 (td, $J = 12.4$, 2.8 Hz, 1H), 2.02 (td, $J = 13.2$, 4.4 Hz, 1H), 1.86 (dt, $J = 13.6$, 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, d$_6$-DMSO) δ 149.0, 144.8, 136.7, 134.5, 133.7, 129.9, 128.2, 128.1, 123.4, 118.5, 113.9, 113.2, 56.9, 51.1, 50.6, 43.7, 36.0. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3396, 2848, 2321, 1604, 1584, 1488, 1446, 1330, 1258, 1227, 1165, 1139, 1091, 1022, 963, 911, 799, 767, 732, 685, 618, 571, 518; HRMS (ESI) calcd for C$_{19}$H$_{20}$ClN$_2$O$_2$S [M+H]$^+$: 375.0929. Found: 375.0927.
3n: (3n) was purified by PE/EtOAc = 1:1) white solid, 48.6 mg, 66% yield, M.P. = 157-158 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84-7.81 (m, 2H), 7.67-7.62 (m, 1H), 7.59-7.55 (m, 2H), 6.68-6.61 (m, 2H), 6.53 (d, $J$ = 2.4 Hz, 1H), 5.03 (s, 1H), 4.57 (s, 1H), 4.28 (dd, $J$ = 13.2, 1.6 Hz, 1H), 3.89-3.84 (m, 1H), 3.73 (s, 3H), 3.34 (AB, $J_{AB}$ = 9.2 Hz, 1H), 3.31 (BA, $J_{BA}$ = 9.2 Hz, 1H) 3.20 (d, $J$ = 13.2 Hz, 1H), 2.62 (td, $J$ = 12.4, 2.8 Hz, 1H), 2.04 (td, $J$ = 12.4, 4.8 Hz, 1H), 1.82 (dt, $J$ = 13.6, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.7, 144.5, 143.5, 136.4, 134.1, 132.9, 129.1, 127.8, 113.8, 113.7, 111.4, 110.7, 57.7, 55.9, 50.8, 50.7, 43.7, 35.5. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3379, 2956, 2931, 2845, 1495, 1464, 1441, 1339, 1291, 1211, 1166, 1109, 1033, 962, 863, 811, 768, 730, 696, 629, 601, 564, 455; HRMS (ESI) calcd for C$_{20}$H$_{23}$N$_2$O$_3$S [M+H]$^+$: 371.1424. Found: 371.1426.

3o: (3o) was purified by PE/EtOAc = 1:1) white solid, 58.6 mg, 66% yield, M.P. = 123-124 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84-7.84 (m, 2H), 7.65-7.61 (m, 1H), 7.58-7.54 (m, 2H) 7.43-7.30 (m, 5H), 6.74 (dd, $J$ = 8.4, 2.4 Hz, 1H), 6.61 (dd, $J$ = 5.2, 2.8 Hz, 2H), 5.01 (s, 1H), 4.97 (s, 2H), 4.55 (s, 1H), 4.27 (dd, $J$ = 13.2, 1.2 Hz, 1H), 3.87-3.84 (m, 1H), 3.34 (AB, $J_{AB}$ = 9.2 Hz, 1H), 3.30 (BA, $J_{BA}$ = 9.2 Hz, 1H) 3.19 (d, $J$ = 13.2 Hz, 1H), 2.91 (brs, 1H), 2.62 (td, $J$ = 12.4, 2.8 Hz, 1H), 2.02 (td, $J$ = 13.2, 4.4 Hz, 1H), 1.82 (dt, $J$ = 13.6, 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.7, 144.7, 143.5, 137.2, 136.3, 134.0, 132.8, 129.1, 128.4, 127.8, 127.7, 127.5, 115.2, 113.7, 112.1, 111.3, 71.0, 57.6, 50.7, 50.7, 43.6, 35.5. IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 3394, 3357, 2921, 2828, 1646, 1594, 1493, 1446, 1336, 1224, 1196, 1163, 1092, 1017, 916, 864, 802, 754, 694, 626, 573; HRMS (ESI) calcd for C$_{26}$H$_{27}$N$_2$O$_3$S [M+H]$^+$: 447.1737. Found: 447.1741.
3p: (3p) was purified by PE/EtOAc = 2:1) white solid, 56.2 mg, 78% yield, M.P. = 164-166 °C. 1H NMR (400 MHz, CDCl₃) δ 7.83-7.81 (m, 2H), 7.66-7.63 (m, 1H), 7.59-7.55 (m, 2H), 6.77 (td, J = 8.4, 2.4 Hz, 1H), 7.61 (dd, J = 8.8, 2.8 Hz, 1H), 6.57 (dd, J = 8.4, 4.4 Hz, 1H) 5.04 (s, 1H), 4.56 (s, 1H), 4.28 (dd, J = 13.2, 2.0 Hz, 1H), 3.88-3.82 (m, 1H), 3.60 (brs, 1H), 3.38 (AB, J_AB = 9.2 Hz, 1H), 3.33 (BA, J_BA = 9.2 Hz, 1H), 3.19 (d, J = 13.2 Hz, 1H), 2.62 (td, J = 12.4, 2.8 Hz, 1H), 1.98 (td, J = 13.6, 4.8 Hz, 1H), 1.82 (dt, J = 13.6, 2.8 Hz, 1H). 19F NMR (376 MHz, CDCl₃) δ -125.2 (m). 13C NMR (100 MHz, CDCl₃) δ 156.9 (d, J = 234.9 Hz), 146.8, 143.3, 136.3, 134.0 (d, J = 7.4 Hz), 132.9, 129.1, 127.7, 114.7 (d, J = 23.3 Hz), 113.8, 111.7 (d, J = 23.9 Hz), 110.7 (d, J = 8.1 Hz), 57.7, 50.60, 50.57, 43.5, 35.5. IR (thin film): ν_max (cm⁻¹) = 3388, 3061, 2958, 2926, 2858, 1728, 1653, 1610, 1585, 1490, 1447, 1338, 1290, 1165, 1093, 913, 804, 764, 727, 694, 625, 579, 535, 465; HRMS (ESI) calcd for C₁₉H₂₀FN₂O₂S [M+H]^+: 359.1224. Found: 359.1226.

3q: (3q) was purified by PE/EtOAc = 2:1) white solid, 63.5 mg, 76% yield, M.P. = 163-164 °C. 1H NMR (400 MHz, CDCl₃) δ 7.83-7.80 (m, 2H), 7.67-7.63 (m, 1H), 7.59-7.55 (m, 2H), 7.14 (dd, J = 8.4, 2.0 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 5.04 (s, 1H), 4.58 (s, 1H), 4.27 (dd, J = 13.2, 1.6 Hz, 1H), 3.86-3.81 (m, 1H), 3.72 (brs, 1H), 3.38 (AB, J_AB = 9.2 Hz, 1H), 3.32 (BA, J_BA = 9.2 Hz, 1H), 3.19 (d, J = 13.2 Hz, 1H), 2.63 (td, J = 12.8, 3.2 Hz, 1H), 1.96 (td, J = 13.2, 4.4 Hz, 1H), 1.80 (dt, J = 13.6, 2.8 Hz, 1H). 13C NMR (100 MHz, CDCl₃) δ 149.9, 143.2, 136.3, 134.5, 133.0, 131.0, 129.1, 127.7, 127.5, 113.9, 111.4, 110.2, 57.4, 50.6, 50.3, 43.4, 35.6. IR (thin film): ν_max (cm⁻¹) = 3391, 2923, 2849, 1600, 1485, 1444, 1336, 1287, 1259, 1168, 1127, 1090, 1025, 960, 806, 880, 815, 773, 726, 693, 626, 602, 576, 553, 463; HRMS (ESI)
calcd for C$_{19}$H$_{20}$BrN$_2$O$_2$S [M+H]$^+$: 419.0423. Found: 419.0423.

3. References


4. X-Ray crystal data of 2n (CCDC 1915944), 3a (CCDC 1915943) (The crystal was obtained by slow evaporation of products in DCM)

Crystal data and structure refinement for mjl18429_0m.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>mjl18429_0m</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C26.50 H25 Cl N2 O2 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>470.99</td>
</tr>
<tr>
<td>Temperature</td>
<td>169.99 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.34139 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 1 21/n 1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>16.7555(3) Å</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90°</td>
</tr>
<tr>
<td>b</td>
<td>14.8460(3) Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>93.2460(10)°</td>
</tr>
<tr>
<td>c</td>
<td>18.5857(3) Å</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90°</td>
</tr>
<tr>
<td>Volume</td>
<td>4615.81(15) Å</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.356 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.657 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1976</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.12 x 0.08 x 0.05 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.006 to 54.921°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-20&lt;=$h$&lt;=$20$, -17&lt;=$k$&lt;=$18$, -22&lt;=$l$&lt;=$22$</td>
</tr>
</tbody>
</table>
Reflections collected: 39637
Independent reflections: 8727 [R(int) = 0.0465]
Completeness to theta = 53.594°: 99.6%
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.7508 and 0.5978
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 8727 / 7 / 588
Goodness-of-fit on F^2: 1.038
Final R indices [I>2sigma(I)]:
R1 = 0.0622, wR2 = 0.1647
R indices (all data):
R1 = 0.0755, wR2 = 0.1759
Extinction coefficient: n/a
Largest diff. peak and hole: 1.433 and -1.037 e.Å^{-3}

Crystal data and structure refinement for mo_d8v18765_0m.

Identification code: mo_d8v18765_0m
Empirical formula: C20 H22 N2 O2 S
Formula weight: 354.45
Temperature: 296(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: P 21/n
Unit cell dimensions:
\[ a = 11.6381(5) \text{ Å} \quad \alpha = 90°. \]
\[ b = 8.1637(2) \text{ Å} \quad \beta = 100.0880(10)°. \]
\[ c = 19.3121(7) \text{ Å} \quad \gamma = 90°. \]
Volume: 1806.47(11) Å^3
Z: 4
Density (calculated): 1.303 Mg/m^3
Absorption coefficient: 0.195 mm^{-1}
F(000): 752
Crystal size: 0.200 x 0.170 x 0.140 mm^3
Theta range for data collection: 3.390 to 25.999°.
<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Index ranges</td>
<td>-11 ≤ h ≤ 14, -8 ≤ k ≤ 10, -23 ≤ l ≤ 19</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>8712</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3516 [R(int) = 0.0240]</td>
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<tr>
<td>Completeness to theta = 25.242°</td>
<td>98.8%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.7456 and 0.6492</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0440, wR₂ = 0.1117</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0560, wR₂ = 0.1216</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.273 and -0.297 e.Å⁻³</td>
</tr>
</tbody>
</table>
5. Copies of NMR spectra

Figure 1 $^1$H NMR spectrum of 1a (400 MHz, CDCl$_3$)
Figure 2 $^1$H NMR spectrum of 1b (400 MHz, CDCl$_3$)
Figure 3 $^1$H NMR spectrum of $1c$ (400 MHz, CDCl$_3$)
Figure 4 $^{13}$C NMR spectrum of 1c (100 MHz, CDCl$_3$)
Figure 5 $^1$H NMR spectrum of 1d (400 MHz, CDCl$_3$)
Figure 6 $^{13}$C NMR spectrum of 1d (100 MHz, CDCl$_3$)
Figure 7 ¹H NMR spectrum of 1e (400 MHz, d₆-DMSO)
Figure 8 $^{13}$C NMR spectrum of 1e (100 MHz, $d_6$-DMSO)
Figure 9 $^1$H NMR spectrum of 1f (400 MHz, CDCl$_3$)
**Figure 10** $^{13}$C NMR spectrum of 1f (100 MHz, CDCl$_3$)
Figure 11 $^1$H NMR spectrum of 1g (400 MHz, CDCl$_3$)
Figure 12 $^{13}$C NMR spectrum of 1g (100 MHz, CDCl$_3$)
Figure 13 $^1$H NMR spectrum of 1h (400 MHz, CDCl$_3$)
Figure 14 $^{13}$C NMR spectrum of 1h (100 MHz, CDCl$_3$)
Figure 15 $^1$H NMR spectrum of 1i (400 MHz, CDCl$_3$)
Figure 16 $^{13}$C NMR spectrum of 1i (100 MHz, CDCl$_3$)
Figure 17 $^1$H NMR spectrum of 1j (400 MHz, CDCl$_3$)
Figure 18 $^{19}$F NMR spectrum of 1j (376 MHz, CDCl$_3$)
Figure 19: $^{13}$C NMR spectrum of 1j (100 MHz, CDCl$_3$)
Figure 20 $^1$H NMR spectrum of 1k (400 MHz, CDCl$_3$)
Figure 21 $^{13}$C NMR spectrum of 1k (100 MHz, CDCl$_3$)
Figure 22 $^1$H NMR spectrum of 11 (400 MHz, CDCl$_3$)
Figure 23. $^{13}$C NMR spectrum of 11 (100 MHz, CDCl$_3$)
Figure 24 $^1$H NMR spectrum of 1m (400 MHz, CDCl$_3$)
Figure 25 $^{13}$C NMR spectrum of 1m (100 MHz, CDCl$_3$)
Figure 26 $^1$H NMR spectrum of 1n (400 MHz, CDCl$_3$)
Figure 27 $^{13}$C NMR spectrum of 1n (100 MHz, CDCl$_3$)
Figure 28 $^1$H NMR spectrum of 4b (400 MHz, CDCl$_3$)
Figure 29 $^1$H NMR spectrum of 4c (400 MHz, CDCl$_3$)
Figure 30 ¹H NMR spectrum of 4d (400 MHz, CDCl₃)
Figure 31 $^1$H NMR spectrum of 4e (400 MHz, CDCl$_3$)
Figure 32 $^{13}$C NMR spectrum of 4e (100 MHz, CDCl$_3$)
Figure 33 $^1$H NMR spectrum of 4f (400 MHz, CDCl$_3$)
Figure 34: $^{13}$C NMR spectrum of 4f (100 MHz, CDCl$_3$)
Figure 35 $^1$H NMR spectrum of 4g (400 MHz, CDCl$_3$)
Figure 36 $^{13}$C NMR spectrum of 4g (100 MHz, CDCl$_3$)
Figure 37 $^1$H NMR spectrum of 4h (400 MHz, CDCl$_3$)
Figure 38 $^{13}$C NMR spectrum of 4h (100 MHz, CDCl₃)
Figure 39 $^1$H NMR spectrum of 4i (400 MHz, CDCl$_3$)
Figure 40 $^{13}$C NMR spectrum of 4i (100 MHz, CDCl$_3$)
Figure 41 $^1$H NMR spectrum of 4j (400 MHz, CDCl$_3$)
Figure 42 $^{13}$C NMR spectrum of 4j (100 MHz, CDCl$_3$)
Figure 43 $^1$H NMR spectrum of 4k (400 MHz, CDCl$_3$)
Figure 44 $^{13}$C NMR spectrum of 4k (100 MHz, CDCl$_3$)
Figure 45 $^1$H NMR spectrum of 4l (400 MHz, CDCl$_3$)
Figure 46 $^{13}$C NMR spectrum of 4l (100 MHz, CDCl$_3$)
Figure 47 \(^1\)H NMR spectrum of 4m (400 MHz, CDCl\(_3\))
Figure 48 $^{13}$C NMR spectrum of 4m (100 MHz, CDCl$_3$)
Figure 49 $^1$H NMR spectrum of 4n (400 MHz, CDCl$_3$)
Figure 50 $^{13}$C NMR spectrum of 4n (100 MHz, CDCl$_3$)
Figure 51 $^1$H NMR spectrum of 4o (400 MHz, CDCl$_3$)
Figure 52 $^{13}$C NMR spectrum of 4o (100 MHz, CDCl$_3$)
Figure 53 $^1$H NMR spectrum of 4p (400 MHz, CDCl$_3$)
Figure 54 $^{19}$F NMR spectrum of 4p (100 MHz, CDCl$_3$)
Figure 55 $^{13}$C NMR spectrum of 4p (100 MHz, CDCl$_3$)
Figure 56 $^1$H NMR spectrum of 4q (400 MHz, CDCl$_3$)
Figure 57 $^{13}$C NMR spectrum of 4q (100 MHz, CDCl$_3$)
Figure 58 $^1$H NMR spectrum of 2b (400 MHz, CDCl$_3$)
Figure 59 $^{13}$C NMR spectrum of 2b (100 MHz, CDCl$_3$)
Figure 60 $^1$H NMR spectrum of 2c (400 MHz, CDCl$_3$)
Figure 61 $^{13}$C NMR spectrum of 2c (100 MHz, CDCl$_3$)
Figure 62 $^1H$ NMR spectrum of 2d (400 MHz, CDCl$_3$)
Figure 63 $^{13}$C NMR spectrum of 2d (100 MHz, CDCl$_3$)
Figure 64 $^1$H NMR spectrum of 2e (400 MHz, CDCl$_3$)
Figure 65 $^{13}$C NMR spectrum of 2e (100 MHz, CDCl$_3$)
Figure 66 $^1$H NMR spectrum of 2f (400 MHz, CDCl$_3$)
Figure 67 $^{13}$C NMR spectrum of 2f (100 MHz, CDCl$_3$)
Figure 68 $^1$H NMR spectrum of 2g (400 MHz, CDCl$_3$)
Figure 69 $^{13}$C NMR spectrum of 2g (100 MHz, CDCl$_3$)
Figure 70 $^1$H NMR spectrum of 2h (400 MHz, CDCl$_3$)
Figure 71 $^{13}$C NMR spectrum of 2h (100 MHz, CDCl$_3$)
Figure 72 $^1$H NMR spectrum of 2i (400 MHz, CDCl$_3$)
Figure 73 $^{13}$C NMR spectrum of 2i (100 MHz, CDCl$_3$)
Figure 74 $^1$H NMR spectrum of 2j (400 MHz, CDCl$_3$)
Figure 75 $^{19}$F NMR spectrum of 2j (376 MHz, CDCl$_3$)
Figure 76 $^{13}$C NMR spectrum of 2j (100 MHz, CDCl$_3$)
Figure 77 $^1$H NMR spectrum of 2k (400 MHz, CDCl$_3$)
Figure 78 $^{13}$C NMR spectrum of 2k (100 MHz, CDCl$_3$)
Figure 79 $^1$H NMR spectrum of 2l (400 MHz, CDCl$_3$)
Figure 80 ¹³C NMR spectrum of 2l (100 MHz, CDCl₃)
Figure 81 $^1$H NMR spectrum of 2m (400 MHz, CDCl$_3$)
Figure 82. $^{13}$C NMR spectrum of 2m (100 MHz, CDCl$_3$)
Figure 83 $^1$H NMR spectrum of 2n (400 MHz, CDCl$_3$)
Figure 84 $^{13}$C NMR spectrum of 2n (100 MHz, CDCl$_3$)
Figure 85 $^1$H NMR spectrum of 3a (400 MHz, CDCl$_3$)
Figure 86 $^{13}$C NMR spectrum of 3a (100 MHz, CDCl$_3$)
Figure 87 $^1$H NMR spectrum of 3b (400 MHz, CDCl$_3$)
Figure 88 $^{13}$C NMR spectrum of 3b (100 MHz, CDCl$_3$)
**Figure 89** $^1$H NMR spectrum of 3c (400 MHz, CDCl$_3$)
Figure 90 $^{13}$C NMR spectrum of 3c (100 MHz, CDCl$_3$)
Figure 91 $^1$H NMR spectrum of 3d (400 MHz, $d_6$-DMSO)
Figure 92 $^{13}$C NMR spectrum of 3d (100 MHz, $d_6$-DMSO)
Figure 93 $^1$H NMR spectrum of 3e (400 MHz, CDCl$_3$)
Figure 94 $^{13}$C NMR spectrum of 3e (100 MHz, CDCl$_3$)
Figure 95 $^1$H NMR spectrum of 3f (400 MHz, CDCl$_3$)
Figure 96: $^{13}$C NMR spectrum of 3f (100 MHz, CDCl$_3$)
Figure 97 $^1$H NMR spectrum of 3g (400 MHz, CDCl$_3$)
Figure 98 $^{13}$C NMR spectrum of 3g (100 MHz, CDCl$_3$)
Figure 99 $^1$H NMR spectrum of 3h (400 MHz, CDCl$_3$)
Figure 100 $^{13}$C NMR spectrum of 3h (100 MHz, CDCl$_3$)
Figure 101 $^1$H NMR spectrum of 3i (400 MHz, CDCl$_3$)
Figure 102 $^{13}$C NMR spectrum of 3i (100 MHz, CDCl$_3$)
Figure 103 $^1$H NMR spectrum of 3j (400 MHz, $d_6$-DMSO)
Figure 104 $^{13}$C NMR spectrum of 3j (100 MHz, $d_6$-DMSO)
Figure 105 $^1$H NMR spectrum of 3k (400 MHz, CDCl$_3$)
Figure 106 $^{13}$C NMR spectrum of 3k (100 MHz, CDCl$_3$)
Figure 107 $^1$H NMR spectrum of 3l (400 MHz, CDCl$_3$)
Figure 108 $^{13}$C NMR spectrum of 3l (100 MHz, CDCl$_3$)
Figure 109 $^1$H NMR spectrum of 3m (400 MHz, CDCl$_3$)
Figure 110 $^{13}$C NMR spectrum of 3m (100 MHz, CDCl$_3$)
Figure 111 $^1$H NMR spectrum of 3n (400 MHz, CDCl$_3$)
Figure 112 $^{13}$C NMR spectrum of 3n (100 MHz, CDCl$_3$)
Figure 113 $^1$H NMR spectrum of 3o (400 MHz, CDCl₃)
Figure 114 $^{13}$C NMR spectrum of 3o (100 MHz, CDCl$_3$)
Figure 115 $^1$H NMR spectrum of 3p (400 MHz, CDCl$_3$)
Figure 116 $^{19}$F NMR spectrum of 3p (376 MHz, CDCl$_3$)
Figure 117 $^{13}$C NMR spectrum of 3p (100 MHz, CDCl$_3$)
Figure 118 $^1$H NMR spectrum of 3q (400 MHz, CDCl$_3$)
Figure 119 $^{13}$C NMR spectrum of 3q (100 MHz, CDCl$_3$)