Supporting Information for

Construction of Spirocarbocycles *via* Gold-Catalyzed Intramolecular Dearomatization of 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. ¹H spectra were recorded on a Varian (300 MHz or 400 MHz) or Agilent instrument (400 MHz) and internally referenced to tetramethylsilane signal or residual solvent signals. ¹³C NMR spectra were recorded on a Varian (100 MHz or 75 MHz) or Agilent instrument (100 MHz) and internally referenced to residual solvent signals. ¹⁹F NMR spectra were recorded on a Varian or Agilent instrument (376 MHz) and referenced relative to CFCl₃. Data for ¹H 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 ¹³C NMR and ¹⁹F NMR are reported in terms of chemical shift (δ , ppm).

General procedure for the preparation of 1-naphthol derivatives (1a-1t)



To a solution of 4-hydroxy-1-naphthaldehyde^[1] (14.15 g, 82 mmol) and imidazole (8.40 g, 123 mmol) in DCM (100 mL), triisopropylsilyl chloride (TIPSCl, 20 mL, 90 mmol) was added dropwise and the mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH₄Cl (100 mL) and extracted with DCM (50 mL x 3). The combined DCM extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by recrystallization (PE) and **S1** was obtained in 77% yield (22.60 g).



To a dry two-necked, round-bottomed flask containing a solution of **S1** (3.28 g, 10 mmol) in THF (50 mL), activated zinc powder (845.0 mg, 13 mmol) was added and 3-bromopropyne (1.65 g, 14 mmol) was added dropwise under argon. The mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH₄Cl (50 mL). THF was removed under reduced pressure. The mixture was extracted with EtOAc (50 mL x 3). The combined EtOAc extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was dissolved in DCM (100 mL) and the mixture was cooled at 0°C. After addition of HSiEt₃ (2.33 g, 20 mmol), CF₃COOH (2.28 g, 20 mmol) was added dropwise. The mixture was warmed up to room temperature and stirred. After completion (monitored by TLC), the reaction mixture was quenched with saturated NaHCO₃ (100 mL) and extracted with DCM (50 mL x 3). The combined DCM extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was quenched with saturated nature of the mixture was warmed up to room temperature and stirred. After completion (monitored by TLC), the reaction mixture was quenched with saturated NaHCO₃ (100 mL) and extracted with DCM (50 mL x 3). The combined DCM extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product **S2** was dissolved in THF (10 mL) and the

mixture was cooled at 0°C. Tetrabutylammonium fluoride (TBAF) (7.7 mL, 1M in THF, 7.7 mmol) was added dropwise and the mixture was stirred at 0°C for 10 min. After completion (monitored by TLC), the reaction mixture was quenched with H₂O (2 mL) and THF was removed under reduced pressure. The mixture was extracted with EtOAc (5 mL x 3). The combined EtOAc extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) and **1a** was obtained in 61% yield (674.9 mg, 3.4 mmol).



White solid. M.P. = 59-61 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.63-7.46 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.52 (s, 1H), 3.27 (t, *J* = 7.6 Hz, 2H), 2.62 (td, *J* = 7.2, 2.4 Hz, 2H), 2.08 (t, *J* = 2.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 132.5, 128.8, 126.5, 126.0, 124.9, 124.7, 123.4, 122.4, 108.1, 84.12, 69.2, 31.6, 20.0. IR (thin film): v_{max} (cm⁻¹) = 3670, 3280, 2920, 2113, 1646, 1586, 1514, 1437, 1382, 1336, 1277, 1252, 1143, 1047, 976, 833, 814, 762, 658, 637; HRMS (EI) calcd for C₁₄H₁₂O [M]⁺: 196.0888. Found: 196.0892.



To a dry two-necked, round-bottomed flask containing a solution of 1-(t-butyldimethylsiloxy)-4-iodonaphthalene^[2] (7.69 g, 20 mmol), CuI (1.52 g, 8 mmol), picolinic acid (1.97 g, 16 mmol), and Cs₂CO₃ (19.55 g, 60 mmol) in dioxane (20 mL), diethyl malonate (6.41 g, 20 mmol) was added dropwise under argon^[3]. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH₄Cl (100 mL). dioxane was removed under reduced pressure. The

mixture was extracted with EtOAc (50 mL x 3). The combined EtOAc extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was dissolved in THF (20 mL). The solution was cooled at 0°C and NaH (60% in mineral, 40.2 mg, 1.68 mmol) was added under argon. After the mixture was stirred for 1 h, 3-bromopropyne (2.31 g, 1.94 mmol) was added dropwise. The mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH₄Cl (50 mL) and THF was removed under reduced pressure. The mixture was extracted with EtOAc (50 mL x 3). The combined EtOAc extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was used directly without further purification. Analogous to **1a**, **1b** was obtained in 58% yield for 2 steps after the treatment of TBAF.



White solid. M.P. = 89-90 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.46-7.35 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.73 (brs, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.33-4.21 (m, 4H), 3.43 (d, *J* = 1.6 Hz, 2H), 2.02 (s, 1H), 1.18 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 152.4, 132.0, 126.2, 126.1, 125.3, 124.4, 124.0, 122.8, 107.4, 79.8, 71.4, 62.3, 62.1, 26.9, 13.7. IR (thin film): v_{max} (cm⁻¹) = 3386, 3295, 2978, 1730, 1712, 1626, 1585, 1518, 1441, 1349, 1294, 1243, 1202, 1151, 1090, 1046, 1026, 1006, 957, 857, 836, 807, 763, 720, 677, 642; HRMS (ESI) calcd for C₂₀H₂₁O₅ [M+H]⁺: 341.1384. Found: 341.1382.



A flame-dried two-necked, round-bottomed flask was cooled down to room temperature under argon. To this flask were added $Pd(PPh_3)_4$ (750.0 mg, 0.65 mmol), Na_2CO_3 (2.80 g, 26.4 mmol), DME (30 mL), MeOH (10 mL) and H_2O (10 mL). The reaction mixture was stirred at room temperature for 10 min. Then (4-bromonaphthalen-1-yloxy)(tert-butyl)dimethylsilane^[4] (5.00 g, 13.2 mmol) and (2-formylphenyl)boronic acid (2.20 g, 14.5 mmol) were added. The resulting solution was heated to reflux. After completion (monitored by TLC), the reaction mixture was filtrated through celite and the solvent was removed under reduced pressure. The crude product was used without further purification.

A flame-dried two-necked, round-bottomed flask was cooled down to room temperature under argon. After CBr₄ (2.76 g, 8.32 mmol) was dissolved in DCM (25 mL), PPh₃ (4.36 g, 16.64 mmol) was added at 0°C. Then the above crude product in 10 mL DCM was added dropwise and the solution was warmed up to room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated NaHCO₃ (100 mL) and extracted with DCM (10 mL x 3). The combined DCM extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was used without further purification.

A flame-dried two-necked, round-bottomed flask was cooled down to room temperature under argon. To a solution of the above crude product in THF (30 mL) at -78° C, ^{*n*}BuLi (2.75 mL, 6.6 mmol, 2.4 M in hexane) was added dropwise. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH₄Cl (30 mL) and extracted with EtOAc (10 mL x 3). The combined EtOAc extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was used without further purification. Following the previous procedure by treatment of TBAF, **1c** was obtained in 51% yield (372.0 mg, 1.52 mmol) for 2 steps.



Brown solid. M.P. = 130-131 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.50 (t, J = 6.8 Hz, 1H),

7.46-7.43 (m, 2H), 7.41-7.34 (m, 2H), 7.29 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 5.38 (s, 1H), 2.78 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.1, 143.4, 133.1, 132.9, 131.2, 131.1, 128.5, 127.2, 127.1, 126.4, 126.1, 125.1, 124.1, 122.6, 121.7, 107.9, 82.8, 80.2. IR (thin film): v_{max} (cm⁻¹) = 3672, 3477, 3259, 2986, 2902, 2348, 2322, 1940, 1584, 1513, 1405, 1372, 1339, 1246, 1221, 1048, 894, 819, 764, 665, 631; HRMS (EI) calcd for C₁₈H₁₂O [M]⁺: 244.0888. Found: 244.0887.

1d was prepared following the procedure for the preparation of 1a.



Brown solid. M.P. = 94-95 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.19-8.17 (m, 1H), 7.95-1.92 (m, 1H), 7.52-7.45 (m, 2H), 7.14 (s, 1H), 5.02 (s, 1H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.58 (td, *J* = 8.0, 2.8 Hz, 2H), 2.40 (s, 3H), 2.03 (t, *J* = 2.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 131.1, 129.3, 128.4, 125.4, 125.0, 124.7, 123.3, 121.7, 115.7, 84.1, 69.0, 31.6, 20.1, 15.6. IR (thin film): v_{max} (cm⁻¹) = 3673, 3418, 3284, 2987, 2901, 2115, 1580, 1511, 1384, 1289, 1244, 1151, 1066, 927, 881, 744, 637; HRMS (EI) calcd for C₁₅H₁₄O [M]⁺: 210.1045. Found: 210.1040.



1e and **1f** were prepared from **S2** according to known literature^[5] and subsequent removal of the TIPS protection group, and **1e** and **1f** were obtained in 87% and 44% yield for 2 steps, respectively.



White solid. M.P. = 71-72 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.59-7.48 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.19-5.14 (m, 1H), 3.24 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.4, 132.5, 128.7, 126.5, 126.0, 125.0, 124.6, 123.4, 122.4, 108.1, 79.8, 38.9, 31.5, 21.3. IR (thin film): v_{max} (cm⁻¹) =3303, 3064, 3045, 2926, 2872, 2852, 1946, 1628, 1586, 1515, 1462, 1428, 1398, 1379, 1355, 1282, 1251, 1219, 1185, 1143, 1047, 1018, 975, 815, 759, 741, 619; HRMS (EI) calcd for C₁₄H₁₁OBr [M]⁺: 273.9993. Found: 273.9997.



White solid. M.P. = 78-79 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.29-8.23 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.59-7.50 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.37 (s, 1H), 3.26 (t, *J* = 7.6 Hz, 2H), 2.81-2.73 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 132.4, 128.7, 126.5, 126.0, 124.9, 124.6, 123.3, 122.3, 108.1, 94.1, 31.6, 22.4. IR (thin film): v_{max} (cm⁻¹) = 3451, 3304, 3064, 3043, 2943, 2924, 2907, 2850, 2186, 1985, 1943, 1915, 1818, 1629, 1586, 1515, 1462, 1428, 1398, 1379, 1354, 1330, 1281, 1251, 1218, 1187, 1143, 1046, 1016, 975, 829, 815, 760, 741, 618; HRMS (EI) calcd for C₁₄H₁₁OI [M]⁺: 321.9855. Found: 321.9854.

General procedure for the preparation of 1g-1t (1g as an example).



To a flame-dried two-necked, round-bottomed flask at room temperature under argon were added **S3** (6.90 g, 19.6 mmol), Pd(PPh₃)₂Cl₂ (701.9 mg, 1.0 mmol), CuI

(571.4 mg, 3.0 mmol), PhI (2.1 mL, 19.6 mmol), and NEt₃ (100 mL). The resulting reaction mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was diluted by EtOAc (100 mL), neutralized by 1M HCl (100 mL) and extracted with EtOAc (50 mL x 3). The combined EtOAc extract was washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was used without further purification. Following the previous procedure on removing the TIPS group by the treatment of TBAF, **1g** was obtained in 66% yield (3.52 g) for 2 steps.



White solid. 66% yield for 2 steps. M.P. = 82-83 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.58-7.49 (m, 2H), 7.38-7.36 (m, 2H), 7.29-7.25 (m, 4H), 6.77 (d, J = 7.6 Hz, 1H), 5.16 (d, J = 6.8 Hz, 1H), 3.33 (t, J = 7.6 Hz, 2H), 2.80 (t, J = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 132.7, 131.5, 129.2, 128.2, 127.6, 126.5, 126.2, 124.9, 124.7, 123.8, 123.6, 122.3, 108.1, 89.7, 81.5, 31.9, 21.2. IR (thin film): v_{max} (cm⁻¹) = 3669, 3333, 2984, 1627, 1585, 1514, 1485, 1439, 1379, 1353, 1240, 1143, 1048, 1017, 908, 828, 751, 686; HRMS (ESI) calcd for C₂₀H₁₇O [M+H]⁺: 273.1274. Found: 273.1275.



White solid. 60% yield for 2 steps. M.P. = 96-97 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 6.8 Hz, 1H), 7.48 (t, J = 6.8 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 7.6 Hz, 1H), 5.47 (s, 1H), 3.77 (s, 3H), 3.29 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 150.3, 132.8, 132.7, 129.2, 126.4, 126.1, 124.8, 124.7, 123.6, 122.3, 116.0, 113.8, 108.1, 88.2, 81.2, 55.2, 32.0, 21.1. IR (thin film): v_{max} (cm⁻¹) = 3350, 2996, 2928, 2833, 1628, 1602, 1584, 1508,

1440, 1381, 1354, 1289, 1245, 1170, 1148, 1103, 1048, 1030, 828, 756, 702, 661, 629; HRMS (EI) calcd for C₂₁H₁₈O₂ [M]⁺: 302.1307. Found: 302.1315.



White solid. 69% yield for 2 steps. M.P. = 104-105 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.18 (m, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.55-7.41 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 7.6 Hz, 1H), 5.44 (s, 1H), 3.28 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 137.6, 132.6, 131.3, 129.1, 128.9, 126.4, 126.1, 124.8, 124.6, 123.5, 122.3, 120.6, 108.1, 89.0, 81.6, 31.9, 21.4, 21.1. IR (thin film): v_{max} (cm⁻¹) = 3687, 3381, 2910, 2321, 1910, 1849, 1835, 1628, 1600, 1584, 1510, 1474, 1452, 1426, 1406, 1379, 1354, 1292, 1261, 1241, 1144, 1105, 1060, 1047, 1017, 946, 830, 816, 755, 703; HRMS (EI) calcd for C₂₁H₁₈O [M]⁺: 286.1358. Found: 286.1361.



White solid. 62% yield for 2 steps. M.P. = 108-109 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.62-7.49 (m, 2H), 7.36 (t, *J* = 6.0 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.46 (s, 1H), 3.34 (t, *J* = 7.2 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0 (d, *J* = 247.0 Hz), 160.8, 150.3, 133.2 (d, *J* = 8.1 Hz), 132.6, 129.0, 126.5, 126.1, 124.9, 124.7, 123.5, 122.3, 119.8 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 21.8 Hz), 108.1, 89.4 (d, *J* = 1.4 Hz), 80.5, 31.8, 21.0. ¹⁹F NMR (386 MHz, CDCl₃) δ -114.2 (m). IR (thin film): v_{max} (cm⁻¹) = 3353, 2939, 2321, 1628, 1596, 1584, 1503, 1474, 1380, 1354, 1334, 1291, 1264, 1220, 1147, 1089, 1046, 1015, 972, 832, 759, 703, 659; HRMS (EI) calcd for C₂₀H₁₅OF [M]⁺: 290.1107. Found: 290.1108.



White solid. 70% yield for 2 steps. M.P. = 104-105 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.60-7.50 (m, 2H), 7.31-7.23 (m, 5H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.49 (s, 1H), 3.33 (t, *J* = 7.6 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 133.5, 132.7, 132.6, 128.9, 128.4, 126.5, 126.1, 124.9, 124.7, 123.5, 122.9, 122.3, 108.1, 90.8, 80.5, 31.7, 21.1. IR (thin film): v_{max} (cm⁻¹) = 3517, 2926, 2906, 1910, 1623, 1584, 1514, 1488, 1473, 1397, 1379, 1351, 1286, 1264, 1242, 1205, 1141, 1089, 1046, 1012, 974, 826, 772, 702, 636, 619; HRMS (EI) calcd for C₂₀H₁₅OCl [M]⁺: 306.0811. Found: 306.0816.



White solid. 41% yield for 2 steps. M.P. = 108-109 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.28-8.24 (m, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.58-7.50 (m, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.26-7.20 (m, 3H), 6.77 (d, J = 7.6 Hz, 1H), 5.37 (s, 1H), 3.32 (t, J = 7.6 Hz, 2H), 2.79 (t, J = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.4, 133.0, 132.6, 131.4, 129.0, 126.5, 126.1, 124.9, 124.7, 123.5, 122.7, 122.4, 121.7, 108.1, 91.0, 80.6, 31.7, 21.2. IR (thin film): v_{max} (cm⁻¹) = 3518, 2905, 2360, 1973, 1907, 1847, 1734, 1649, 1623, 1583, 1513, 1483, 1394, 1378, 1350, 1286, 1263, 1241, 1204, 1140, 1068, 1045, 1006, 976, 822, 772, 701, 635, 618; HRMS (EI) calcd for C₂₀H₁₅OBr [M]⁺: 350.0306. Found: 350.0309.



Yellow solid. 78% yield for 2 steps. M.P. = 119-120 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.61-7.48 (m, 4H), 7.39 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 5.50-5.27 (br, 1H),

3.32 (t, J = 7.6 Hz, 2H), 2.83 (t, J = 7.6 Hz, 2H). ¹³C NMR (100 MHz, d6-acetone) δ 153.0, 133.6, 132.9, 132.8, 129.5, 128.0 127.7, 127.0, 126.1, 125.1, 124.2, 123.6, 119.0, 111.6, 108.3, 95.7, 81.0, 31.9, 21.7. IR (thin film): v_{max} (cm⁻¹) = 3417, 2923, 2537, 2321, 2225, 1965, 1925, 1824, 1624, 1600, 1585, 1514, 1499, 1475, 1380, 1338, 1263, 1243, 1214, 1175, 1143, 1104, 1045, 1016, 974, 837, 762, 702; HRMS (EI) calcd for C₂₁H₁₅NO [M]⁺: 297.1154. Found: 297.1149.



Yellow solid. 67% yield for 2 steps. M.P. = 134-135 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.69 (s, 1H), 3.92 (s, 3H), 3.33 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.6, 132.7, 131.4, 129.4, 128.8, 128.75, 128.73, 126.5, 126.2, 124.9, 124.8, 123.5, 122.5, 108.0, 93.3, 81.1, 52.2, 31.7, 21.2. IR (thin film): v_{max} (cm⁻¹) = 3426, 2901, 2321, 2218, 1939, 1828, 1696, 1626, 1602, 1588, 1557, 1514, 1435, 1404, 1381, 1336, 1310, 1292, 1247, 1193, 1173, 1146, 1118, 1047, 959, 857, 821, 768, 748, 697; HRMS (ESI) calcd for C₂₂H₂₂NO [M+NH₄]⁺: 348.1594. Found: 348.1598.



White solid. 43% yield for 2 steps. M.P. = 114-115 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26-8.21 (m, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.58-7.45 (m, 2H), 7.34 (dd, J = 7.6, 1.6 Hz, 1H), 7.28-7.26 (m, 1H), 7.25-7.23 (m, 1H), 6.91-6.85 (m, 2H), 6.77 (d, J = 7.6 Hz, 1H), 5.25 (s, 1H), 3.88 (s, 3H), 3.35 (t, J = 8.0 Hz, 2H), 2.86 (t, J = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 150.3, 133.7, 132.6, 129.1, 129.0, 126.4, 126.2, 124.8, 124.6, 123.6, 122.3, 120.4, 112.8, 110.4, 108.0, 94.1, 55.7, 32.0, 21.5. IR (thin

film): v_{max} (cm⁻¹) = 3671, 3441, 2974, 2321, 1838, 1624, 1586, 1516, 1490, 1453, 1431, 1407, 1377, 1350, 1283, 1257, 1182, 1151, 1115, 1047, 1016, 974, 933, 895, 825, 793, 758, 742, 707; HRMS (EI) calcd for $C_{21}H_{18}O_2$ [M]⁺: 302.1307. Found: 302.1305.



White solid. 63% yield for 2 steps. M.P. = 99-100 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.59-7.48 (m, 2H), 7.24 (s, 1H), 7.20-7.15 (m, 3H), 7.09 (t, *J* = 4.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.19 (s, 1H), 3.32 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 137.8, 132.6, 132.1, 129.1, 128.51,128.49, 128.1, 126.5, 126.1, 124.9, 124.7, 123.54, 123.50, 122.3, 108.1, 89.4, 81.6, 31.9, 21.2, 21.1. IR (thin film): v_{max} (cm⁻¹) = 3275, 3033, 2911, 2321, 2226, 1628, 1599, 1583, 1515, 1480, 1443, 1379, 1354, 1301, 1273, 1248, 1218, 1142, 1091, 1045, 1017, 970, 901, 875, 827, 780, 756, 687; HRMS (EI) calcd for C₂₁H₁₈O [M]⁺: 286.1358. Found: 286.1353.



White solid. 70% yield for 2 steps. M.P. = 76-77 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.92-7.85 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 6.8 Hz, 1H), 7.63-7.50 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.58 (s, 1H), 3.47 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.4, 133.4, 133.1, 132.6, 130.0, 129.0, 128.1, 128.0, 126.5, 126.4, 126.33, 126.29, 126.2, 125.2, 124.9, 124.7, 123.5, 122.4, 121.4, 108.1, 94.7, 79.6, 31.9, 21.3. IR (thin film): v_{max} (cm⁻¹) = 3672, 3285, 2986, 2321, 1925, 1627, 1586, 1514, 1443, 1380, 1355, 1338, 1274, 1250, 1220, 1143, 1047, 971, 902, 825, 795, 759; HRMS (EI) calcd for



Yellow solid. 56% yield for 2 steps. M.P. = 164-165 °C. ¹H NMR (400 MHz, d6-DMSO) δ 10.07 (s, 1H), 8.29 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 3.6 Hz, 1H), 7.59 (s, 1H), 7.57-7.43 (m, 2H), 7.34-7.26 (m, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 3.2 Hz, 1H), 3.25 (t, J = 7.2 Hz, 2H), 2.78 (t, J = 7.2 Hz, 2H), 2.63 (s, 3H). ¹³C NMR (100 MHz, d6-DMSO) δ 169.6, 152.2, 134.1, 132.4, 130.4, 128.2, 127.7, 126.9, 126.6, 126.2, 125.0, 124.2, 123.7, 123.5, 122.7, 118.2, 116.0, 107.9, 107.5, 89.1, 81.9, 31.1, 23.8, 20.7. IR (thin film): v_{max} (cm⁻¹) = 3183, 3150, 2937, 1671, 1622, 1584, 1542, 1517, 1467, 1440, 1380, 1351, 1330, 1276, 1262, 1217, 1182,1148, 1089, 1047, 1016, 941, 874, 825, 816, 766, 712, 638; HRMS (ESI) calcd for C₂₄H₂₀NO₂ [M+H]⁺: 354.1489. Found: 354.1487.



White solid. 66% yield for 2 steps. M.P. = 63-64 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 6.8 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 7.13 (d, *J* = 3.2 Hz, 1H), 6.96 (t, *J* = 4.0 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.46 (s, 1H), 3.33 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.4, 132.6, 131.0, 128.9, 126.8, 126.5, 126.2, 126.0, 124.9, 124.7, 123.9, 123.5, 122.4, 108.1, 93.8, 74.7, 31.7, 21.4. IR (thin film): v_{max} (cm⁻¹) = 3273, 3100, 2916, 2843, 2321, 2223, 1840, 1808, 1625, 1583, 1515, 1475, 1438, 1383, 1334, 1269, 1252, 1237, 1213, 1187, 1139, 1062, 1044, 1024, 972, 847, 826, 768,741, 708; HRMS (EI) calcd for C₁₈H₁₄OS [M]⁺: 278.0765. Found: 278.0766.



White solid. 65% yield for 2 steps. M.P. = 165-166 °C. ¹H NMR (400 MHz, d6-DMSO) δ 10.02 (s, 1H), 8.50 (d, *J* = 4.8 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.74 (td, *J* = 7.6, 1.6 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.24 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (100 MHz, d6-DMSO) δ 152.2, 149.9, 142.9, 136.6, 132.3, 126.9, 126.3, 124.9, 124.2, 123.4, 122.9, 122.7, 107.5, 90.2, 81.5, 30.7, 20.3. IR (thin film): v_{max} (cm⁻¹) = 2943, 2577, 2221, 1623, 1583, 1517, 1466, 1432, 1383, 1359, 1273, 1247, 1220, 1152, 1050, 1015, 967, 824, 772, 757, 734, 635; HRMS (EI) calcd for C₁₉H₁₅NO [M]⁺: 273.1154. Found: 273.1152.



Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 5.51 (s, 1H), 3.87 (s, 3H), 3.33-3.20 (m, 2H), 2.49-2.41 (m, 2H), 2.00 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.5, 151.4, 133.4, 127.1, 122.9, 122.5, 121.9, 119.9, 114.1, 97.5, 84.8, 68.3, 56.3, 24.0, 19.0. IR (thin film): v_{max} (cm⁻¹) = 3290, 3069, 2939, 2845, 2115, 1626, 1590, 1518, 1456, 1379, 1362, 1292, 1232, 1173, 1150, 1111, 1071, 1025, 997, 824, 760, 632; HRMS (EI) calcd for C₁₅H₁₄O₂ [M]⁺: 226.0994. Found: 226.0990.



White solid. M.P. = 82-83 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.59-7.48 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H),

Hz, 1H), 5.93 (s, 1H), 5.00 (s, 2H), 4.21 (d, J = 2.4 Hz, 2H), 2.54 (t, J = 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 133.1, 128.3, 126.9, 125.1, 124.8, 124.4, 124.0, 122.2, 107.6, 79.5, 75.0, 69.8, 56.6. IR (thin film): v_{max} (cm⁻¹) = 3285, 3209, 2953, 2931, 2866, 1582, 1516, 1384, 1352, 1278, 1224, 1152, 1043, 953, 879, 826, 767, 698, 671, 630; Anal. calcd for C₁₄H₁₂O₂: C, 79.22; H, 5.70; Found: C, 79.03; H, 5.75.

White solid. M.P. = 46-47 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.37 (s, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.45 (dt, *J* = 7.2, 2.8 Hz, 2H), 2.01 (t, *J* = 2.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 132.7, 129.6, 115.2, 84.0, 68.9, 33.9, 20.8. IR (thin film): v_{max} (cm⁻¹) = 3280, 3201, 2930, 2115, 1888, 1660, 1610, 1511, 1444, 1363, 1288, 1232, 1170, 1100, 1015, 849, 832, 776, 646; HRMS (EI) calcd for C₁₀H₁₀O [M]⁺: 146.0732. Found: 146.0735.

OН

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.51 (m, 4H), 7.48-7.42 (m, 1H), 7.23-7.16 (m, 2H), 6.98 (d, J = 8.4 Hz, 1H), 5.61 (s, 1H), 2.91 (t, J = 7.6 Hz, 2H), 2.57 (td, J = 7.6, 2.8 Hz, 2H), 2.09 (t, J = 2.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 137.1, 132.6, 130.1, 129.0, 128.8, 128.7, 127.8, 127.5, 115.7, 83.9, 69.0, 33.7, 20.6. IR (thin film): v_{max} (cm⁻¹) = 3519, 3288, 2926, 2321, 2114, 1600, 1504, 1486, 1446, 1416, 1330, 1289, 1269, 1229, 1174, 1125, 1074, 1024, 890, 815, 755, 731, 700, 628; HRMS (EI) calcd for C₁₆H₁₄O [M]⁺: 222.1045. Found: 222.1047.

General procedure for gold-catalyzed dearomatization of naphthols



A flame-dried Schlenk tube was cooled down to room temperature under argon. To this tube were added Ph_3PAuCl (4.9 mg, 0.01 mmol, 0.5 mol%), 1-naphthol derivative **1** (0.2 mmol, 1.0 equiv.), and DCM (2.0 mL), and AgOMs (2.0 mg, 0.01 mmol, 0.5 mol%) was added last. Then the reaction mixture was stirred at room temperature in the dark. After completion (monitored by TLC), the reaction mixture was loaded on the silica column. The crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired product **2**.



Colorless oil. 96% yield (39.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.18-8.13 (m, 1H), 7.56-7.52 (m, 1H), 7.41-7.34 (m, 2H), 6.89 (d, *J* = 10.0 Hz, 1H), 6.37 (d, *J* = 10.0 Hz, 1H), 6.17-6.09 (m, 1H), 5.45-5.39 (m, 1H), 2.81-2.66 (m, 2H), 2.37-2.25 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 153.9, 148.7, 134.9, 134.0, 132.7, 130.9, 127.6, 126.9, 126.2, 54.6, 39.4, 32.8. IR (thin film): v_{max} (cm⁻¹) = 3669, 2968, 2904, 1658, 1599, 1477, 1454, 1390, 1299, 1130, 1061, 968, 918, 841, 766, 742, 708, 681; HRMS (ESI) calcd for C₁₄H₁₃O [M+H]⁺: 197.0961. Found: 197.0962.



Pink solid, M.P. = 58-59 °C. 99% yield (67.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (dd, J = 7.6, 1.2 Hz, 1H), 7.46 (td, J = 7.6, 1.2 Hz, 1H), 7.40-7.33 (m, 2H), 7.25 (d, J = 7.6 Hz, 1H), 6.52 (d, J = 10.4 Hz, 1H), 6.27-6.18 (m, 1H), 5.60-5.52 (m, 1H), 4.24-4.06 (m, 2H), 3.73-3.63 (m, 1H), 3.55 (dt, J = 18.0, 2.0 Hz, 1H), 3.37-3.27 (m,

1H), 3.01-2.92 (m, 1H), 1.20 (t, J = 7.2 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 184.5, 170.1, 168.6, 149.1, 142.3, 133.5, 132.4, 132.1, 131.9, 129.8, 127.9, 127.4, 126.4, 70.0, 61.8, 61.3, 58.8, 41.7, 13.8, 13.1. IR (thin film): v_{max} (cm⁻¹) = 3077, 2989, 2964, 2932, 2901, 2869, 1748, 1727, 1667, 1594, 1453, 1392, 1302, 1235, 1148, 1073, 1050, 1014, 966, 925, 886, 847, 767, 744, 723, 706, 667, 622; HRMS (ESI) calcd for C₂₂H₂₄NO₅ [M+NH₄]⁺: 358.1649. Found: 358.1648.



Yellow solid, M.P. = 98-99 °C. 95% yield (54.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.41-7.28 (m, 3H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 6.41 (d, *J* = 10.0 Hz, 1H), 6.28 (d, *J* = 5.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 185.3, 148.8, 147.4, 144.2, 140.9, 139.7, 134.0, 132.6, 132.0, 129.4, 128.1, 127.6, 126.9, 126.81, 126.77, 123.6, 121.9, 59.1. IR (thin film): v_{max} (cm⁻¹) = 3059, 2923, 2321, 1973, 1659, 1597, 1478, 1452, 1384, 1300, 1268, 1242, 1168, 1150, 1123, 1080, 1002, 945, 879, 845, 771, 758, 735, 676; HRMS (ESI) calcd for C₁₈H₁₃O [M+H]⁺: 245.0961. Found: 245.0962.



Yellowish oil, 44% yield (20.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.21-8.12 (m, 1H), 7.51 (td, J = 8.0, 1.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 6.69 (d, J = 1.2 Hz, 1H), 6.13-6.05 (m, 1H), 5.41 (dt, J = 4.8, 2.0 Hz, 1H), 2.78-2.64 (m, 2H), 2.35-2.21 (m, 2H), 2.01 (d, J = 1.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 185.5, 149.5, 148.9, 135.4, 133.4, 132.3, 132.2, 130.7, 127.4, 126.8, 126.4, 54.2, 39.4, 32.8, 16.3. IR (thin film): v_{max} (cm⁻¹) = 3301, 2946, 2852, 1653, 1598, 1522, 1479, 1455, 1370, 1315, 1274, 1176, 1108, 1042, 1018, 984, 899, 800, 780, 753, 704, 627; HRMS (ESI) calcd for C₁₅H₁₅O [M+H]⁺: 211.1117. Found: 211.1117.



Yellow solid, M.P. = 63-64 °C. 99% yield (54.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, J = 8.0, 1.2 Hz, 1H), 7.58 (td, J = 7.6, 1.2 Hz, 1H), 7.45-7.35 (m, 2H), 6.85 (d, J = 10.0 Hz, 1H), 6.49 (d, J = 10.0 Hz, 1H), 6.28 (t, J = 2.4 Hz, 1H), 2.74-2.60 (m, J = 10.0 Hz, 1Hz), 2.74-2.60 (m, J = 10.0 Hz), 2.60 (m, J = 10.0 Hz), 3.60 (m, J = 10.0 Hz), 3.60 (m, J = 10.0 Hz), 3.60 (m, J =2H), 2.53-2.40 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 184.5, 151.5, 145.9, 134.8, 133.0, 131.5, 128.5, 127.5, 126.8, 126.4, 125.5, 57.7, 39.1, 31.5. IR (thin film): v_{max} $(cm^{-1}) = 3068, 2926, 2855, 1656, 1622, 1598, 1453, 1385, 1298, 1152, 1130, 1056,$ 1018, 991, 926, 853, 835, 758, 677; HRMS (ESI) calcd for C₁₄H₁₂BrO [M+H]⁺: 275.0066. Found: 275.0065.



Yellow solid, M.P. = 78-79 °C. 99% yield (64.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.15 (dd, J = 7.6, 1.2 Hz, 1H), 7.59-7.54 (m, 1H), 7.44-7.39 (m, 1H), 7.32 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 10.0 Hz, 1H), 6.52-6.48 (m, 2H), 2.78-2.60 (m, 2H), 2.44 (t, J = 7.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 184.6, 152.0, 146.6, 143.2, 133.0, 131.5, 128.4, 127.5, 127.0, 126.4, 101.4, 59.9, 38.1, 34.4. IR (thin film): v_{max} (cm⁻¹) = 3025, 2924, 2854, 1730, 1659, 1596, 1476, 1452, 1388, 1301, 1167, 1126, 1064, 1033, 1013, 983, 958, 924, 843, 767, 681; HRMS (ESI) calcd for $C_{14}H_{12}IO [M+H]^+$: 322.9927. Found: 322.9929.



White solid, M.P. = 162-163 °C. 99% yield (45.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, J = 8.4, 1.6 Hz, 1H), 7.50-7.44 (m, 1H), 7.41-7.34 (m, 2H), 7.13 (d, J = 10.0 Hz, 1H), 7.11-7.05 (m, 3H), 7.07-7.00 (m, 2H), 6.58 (t, J = 2.8 Hz, 1H), 6.49 (d, J = 10.0 Hz, 1H), 2.86-2.70 (m, 2H), 2.54-2.45 (m, 1H), 2.37-2.27 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.9, 155.5, 148.0, 145.6, 134.8, 132.9, 131.6, 130.9, 128.1, 127.2, 127.1, 126.9, 126.70, 126.66, 125.9, 56.0, 42.6, 31.1. IR (thin film): v_{max} (cm⁻¹) = 2966, 2933, 2904, 1654, 1597, 1491, 1449, 1388, 1302, 1256, 1152, 1123, 1061, 845, 764, 694; HRMS (ESI) calcd for C₂₀H₁₇O [M+H]⁺: 273.1274. Found: 273.1273.



Yellow solid, M.P. = 98-99 °C. 99% yield (60.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.26-8.22 (m, 1H), 7.48-7.42 (m, 1H), 7.41-7.33 (m, 2H), 7.12 (d, *J* = 10.0 Hz, 1H), 7.00-6.94 (m, 2H), 6.64-6.58 (m, 2H), 6.49 (d, *J* = 10.0 Hz, 1H), 6.45 (t, *J* = 2.4 Hz, 1H), 3.65 (s, 3H), 2.81-2.67 (m, 2H), 2.52-2.41 (m, 1H), 2.33-2.24 (ddd, *J* = m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 158.7, 155.9, 148.2, 145.1, 133.0, 131.0, 129.6, 127.4, 127.14, 127.06, 127.0, 126.7 113.5, 56.1, 55.0, 42.6, 31.1. IR (thin film): v_{max} (cm⁻¹) = 3066, 3037, 3004, 2968, 2931, 2839, 2322, 2297, 1888, 1732, 1651, 1601, 1570, 1507, 1476, 1453, 1387, 1296, 1246, 1179, 1153, 1123, 1111, 1029, 999, 967, 933, 891, 834, 808, 771, 682; HRMS (ESI) calcd for C₂₁H₁₉O₂ [M+H]⁺: 303.1380. Found: 303.1389.



Yellow solid, M.P. = 139-140 °C. 97% yield (55.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.21 (m, 1H), 7.50-7.44 (m, 1H), 7.40-7.35 (m, 2H), 7.13 (d, *J* = 10.0 Hz, 1H), 6.95-6.88 (m, 4H), 6.53 (t, *J* = 2.4 Hz, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 2.83-2.69 (m, 2H), 2.52-2.42 (m, 1H), 2.33-2.24 (m, 1H), 2.21 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 155.7, 148.2, 145.6, 137.2, 133.0, 132.0, 131.0, 130.6, 128.8, 127.1, 126.9, 125.8, 56.1, 42.7, 31.1, 21.0. IR (thin film): v_{max} (cm⁻¹) = 3670, 2970, 2917, 2853,

2321, 1658, 1597, 1567, 1510, 1473, 1452, 1385, 1297, 1251, 1188, 1150, 1124, 1027, 967, 893, 804, 772, 687, 647; HRMS (ESI) calcd for C₂₁H₁₉O [M+H]⁺: 287.1430. Found: 287.1435.



Yellow solid, M.P. = 167-168 °C. 99% yield (58.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.20 (m, 1H), 7.47 (td, *J* = 7.6, 1.6 Hz, 1H), 7.42-7.33 (m, 2H), 7.10 (d, *J* = 10.0 Hz, 1H), 7.02-6.94 (m, 2H), 6.81-6.71 (m, 2H), 6.54-6.43 (m, 2H), 2.84-2.67 (m, 2H), 2.52-2.42 (m, 1H), 2.37-2.26 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.8, 163.2 (d, *J* = 246.0 Hz), 160.7, 155.2, 147.8, 144.7, 133.0, 131.5, 131.4, 131.03, 131.00, 127.6 (d, *J* = 7.8 Hz), 127.3, 127.1, 126.8, 126.7, 115.0 (d, *J* = 21.4 Hz), 56.1, 42.7, 31.1; ¹⁹F NMR (386 MHz, CDCl₃) δ -114.3 (m). IR (thin film): v_{max} (cm⁻¹) = 3055, 2942, 2854, 2321, 1914, 1650, 1598, 1503, 1476, 1453, 1388, 1299, 1261, 1245, 1218, 1153, 1124, 1100, 1064, 1032, 1017, 1001, 967, 928, 897, 843, 805, 766, 683; HRMS (ESI) calcd for C₂₀H₁₆FO [M+H]⁺: 291.1180. Found: 291.1182.



Yellow solid, M.P. = 112-113 °C. 99% yield (61.1 mg). ¹H NMR (400 MHz, CDCl₃).8 8.25-8.19 (m, 1H), 7.50-7.44 (m, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 10.0 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.55 (t, J = 2.4 Hz, 1H), 6.49 (d, J = 10.4 Hz, 1H), 2.83-2.69 (m, 2H), 2.52-2.42 (m, 1H), 2.362.27 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.8, 155.0, 147.7, 144.7, 133.3, 133.1, 132.3, 131.0, 128.3, 127.4, 127.23, 127.16, 126.9, 126.7, 56.0, 42.7, 31.2. IR (thin film): v_{max} (cm⁻¹) = 3033, 2925, 2348, 1728, 1659, 1598, 1489, 1452, 1385, 1298, 1269, 1152, 1125, 1092, 1064, 1008, 964, 892, 827, 808, 771, 720, 686; HRMS (ESI) calcd for C₂₀H₁₆ClO [M+H]⁺: 307.0884. Found: 307.0888.



Yellow solid, M.P. = 143-144 °C. 99% yield (78.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.6 Hz, 1H), 7.49-7.43 (m, 1H), 7.41-7.30 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 10.0 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.56 (t, *J* = 2.4 Hz, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 2.83-2.67 (m, 2H), 2.52-2.42 (m, 1H), 2.36-2.27 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.7, 155.0, 147.6, 144.7, 133.7, 133.1, 132.4, 131.2, 131.0, 127.5, 127.3, 127.1, 126.8, 126.7, 121.2, 55.9, 42.7, 31.2. IR (thin film): v_{max} (cm⁻¹) = 3093, 3060, 3033, 2941, 2851, 2321, 1733, 1659, 1598, 1568, 1484, 1452, 1385, 1297, 1269, 1167, 1151, 1126, 1109, 1072, 1026, 1005, 961, 891, 840, 825, 807, 773, 753, 714, 685; HRMS (ESI) calcd for C₂₀H₁₆OBr [M+H]⁺: 351.0379. Found: 351.0390.



Yellow solid, M.P. = 154-155 °C. 97% yield (59.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.40-7.27 (m, 4H), 7.12-7.04 (m, 3H), 6.72 (t, J = 2.4 Hz, 1H), 6.49 (d, J = 10.4 Hz, 1H), 2.87-2.74 (m, 2H), 2.54-2.44 (m, 1H), 2.39-2.29 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.4, 154.2, 147.2, 144.4, 139.3, 135.4, 133.2, 131.9, 130.9, 127.6, 127.3, 126.9, 126.5, 126.4, 118.5, 110.6, 55.8, 42.7, 31.3. IR (thin film): v_{max} (cm⁻¹) = 3070, 3037, 2925, 2321, 2219, 1726, 1662, 1625, 1600, 1501, 1453, 1389, 1300, 1262, 1151, 1128, 1101, 1063, 1028, 995, 960, 888, 833, 805, 766, 690; HRMS (ESI) calcd for C₂₁H₁₆NO [M+H]⁺: 298.1226. Found: 298.1228.



Yellow solid, M.P. = 131-133 °C. 96% yield (64.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 10.0 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.69 (t, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 2.84-2.74 (m, 2H), 2.52-2.43 (m, 1H), 2.38-2.28 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.7, 166.5, 154.8, 147.6, 145.1, 139.3, 134.1, 133.0, 131.0, 129.4, 128.7, 127.4, 127.1, 126.8, 126.6, 125.8, 55.9, 51.9, 42.8, 31.3. IR (thin film): v_{max} (cm⁻¹) = 3052, 2922, 2848, 2348, 2321, 1706, 1659, 1605, 1564, 1475, 1451, 1431, 1409, 1388, 1281, 1185, 1165, 1152, 1106, 1018, 999, 968, 890, 850, 823, 783, 766, 703; HRMS (ESI) calcd for C₂₂H₁₉O₃ [M+H]⁺: 331.1329. Found: 331.1332.



Yellow solid, M.P. = 110-111 °C. 99% yield (60.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 7.6 Hz, 1H), 7.49-7.39 (m, 2H), 7.36-7.30 (m, 1H), 7.19 (d, *J* = 10.0 Hz, 1H), 7.09-7.01 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.70 (t, *J* = 2.4 Hz, 1H), 6.67-6.63 (m, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 10.0 Hz, 1H), 3.69 (s, 3H), 2.79 (td, *J* = 7.2, 2.4 Hz, 2H), 2.50-2.38 (m, 1H), 2.34-2.22 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 185.1, 157.1, 156.3, 148.3, 142.3, 135.3, 132.6, 130.9, 128.7, 128.2, 126.8, 126.7, 126.5, 126.3, 124.0, 119.9, 110.6, 57.6, 54.8, 42.4, 31.8. IR (thin film): v_{max} (cm⁻¹) = 3053, 2928, 2849, 2322, 1652, 1596, 1488, 1454, 1390, 1300, 1253, 1179, 1152, 1118, 1052, 1026, 1000, 930, 895, 842, 758, 695; HRMS (ESI) calcd for C₂₁H₁₉O₂ [M+H]⁺: 303.1380. Found: 303.1379.



Yellow solid, M.P. = 116-117 °C. 96% yield (54.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 7.6 Hz, 1H), 7.53-7.45 (m, 1H), 7.44-7.33 (m, 2H), 7.13 (d, *J* = 10.0 Hz, 1H), 7.02-6.85 (m, 3H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.57 (t, *J* = 2.4 Hz, 1H), 6.50 (d, *J* = 10.0 Hz, 1H), 2.85-2.68 (m, 2H), 2.54-2.42 (m, 1H), 2.36-2.25 (m, 1H), 2.18 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 155.7, 148.1, 145.8, 137.6, 134.8, 133.0, 131.4, 130.9, 128.2, 128.0, 127.1, 127.0, 126.8, 126.74, 126.72, 122.9, 56.1, 42.6, 31.1, 21.3. IR (thin film): v_{max} (cm⁻¹) = 3051, 2938, 2322, 1951, 1653, 1599, 1481, 1451, 1385, 1298, 1248, 1152, 1124, 1095, 1031, 968, 928, 883, 841, 800, 780, 766, 699; HRMS (ESI) calcd for C₂₁H₁₉O [M+H]⁺: 287.1430. Found: 287.1436.



Yellow solid, M.P. = 167-168 °C. 91% yield (59.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.53-7.42 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 10.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.2 Hz, 1H), 6.37-6.32 (m, 2H), 3.09-2.93 (m, 2H), 2.69-2.53 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 184.8, 154.2, 147.8, 143.8, 135.7, 133.7, 133.3, 132.7, 132.0, 131.3, 128.4, 127.6, 127.3, 127.1, 127.0, 126.4, 125.8, 125.4, 125.2, 124.6, 123.7, 58.6, 41.4, 32.3. IR (thin film): v_{max} (cm⁻¹) = 3687, 3673, 2972, 2348, 2321, 1656, 1596, 1504, 1453, 1407, 1391, 1300, 1243, 1151, 1127, 1064, 988, 925, 894, 845, 775, 683, 660; HRMS (ESI) calcd for C₂₄H₁₉O [M+H]⁺: 323.1430. Found: 323.1432.



White solid, M.P. = 168-169 °C. 98% yield (69.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.48-7.43 (m, 1H), 7.42-7.34 (m, 2H), 7.30 (d, J = 3.2 Hz, 1H), 7.20-7.15 (m, 2H), 7.08 (s, 1H), 6.58 (t, J = 2.4 Hz, 1H), 6.51 (d, J = 10.0 Hz, 1H), 6.41 (d, J = 3.6 Hz, 1H), 2.83-2.74 (m, 2H), 2.55 (s, 3H), 2.53-2.46 (m, 1H), 2.38-2.29 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 168.3, 155.7, 148.1, 145.9, 134.6, 133.0, 131.2, 131.0, 130.6, 130.1, 127.1, 127.0, 126.78, 126.76, 125.4, 123.6, 118.0, 116.1, 109.1, 56.3, 42.8, 31.1, 23.7. IR (thin film): v_{max} (cm⁻¹) = 3672, 2970, 2348, 2322, 1708, 1652, 1600, 1536, 1461, 1435, 1375, 1323, 1303, 1272, 1222, 1188, 1155, 1039, 935, 887, 829, 765, 728, 705, 630; HRMS (ESI) calcd for C₂₄H₂₀NO₂ [M+H]⁺: 354.1489. Found: 354.1491.



White solid, M.P. = 120-121 °C. 95% yield (52.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, J = 7.6, 1.2 Hz, 1H), 7.53-7.47 (m, 1H), 7.45-7.35 (m, 2H), 7.07 (d, J = 10.0 Hz, 1H), 6.97 (d, J = 4.4 Hz, 1H), 6.66 (dd, J = 4.8, 3.6 Hz, 1H), 6.51-6.44 (m, 2H), 6.34 (d, J = 3.6 Hz, 1H), 2.87-2.70 (m, 2H), 2.54-2.33 (m, 1H), 2.40-2.31 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.8, 154.4, 147.7, 139.8, 137.9, 133.0, 131.2, 130.6, 127.4, 127.2, 127.10, 127.06, 126.6, 124.2, 124.1, 56.4, 41.9, 31.4. IR (thin film): v_{max} (cm⁻¹) = 2935, 2847, 2321, 1657, 1598, 1570, 1515, 1452, 1423, 1390, 1302, 1245, 1168, 1125, 1079, 1029, 988, 966, 933, 847, 815, 770, 695; HRMS (ESI) calcd for C₂₄H₂₀NO₂ [M+H]⁺: 279.0838. Found: 279.0840.



White solid, M.P. = 160-161 °C. 99% yield (54.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 4.4 Hz, 1H), 8.24-8.17 (m, 1H), 7.45-7.40 (m, 1H), 7.38-7.32 (m, 2H), 7.29 (dd, J = 8.0, 2.0 Hz, 1H), 7.16 (d, J = 2.8 Hz, 1H), 7.13 (d, J = 10.0 Hz, 1H),

6.95 (dd, J = 7.6, 4.8 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.49 (d, J = 10.0 Hz, 1H), 2.86-2.74 (m, 2H), 2.55-2.45 (m, 1H), 2.4-2.30 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 155.1, 152.6, 149.3, 148.1, 145.7, 136.2, 136.1 133.0, 131.1, 127.1, 127.0, 126.7, 126.5, 121.9, 120.0, 55.1, 42.6, 31.1. IR (thin film): v_{max} (cm⁻¹) = 3051, 2961, 2933, 2844, 1653, 1586, 1437, 1388, 1303, 1155, 980, 842, 783, 763, 685; HRMS (ESI) calcd for C₁₉H₁₆NO [M+H]⁺: 274.1226. Found: 274,1229.



White solid, M.P. = 88-89 °C. 86% yield (35.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 6.8 Hz, 1H), 7.54-7.48 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.20-6.14 (m, 1H), 5.80 (s, 1H), 5.45-5.38 (m, 1H), 3.79 (s, 3H), 2.78-2.67 (m, 2H), 2.69-2.48 (m, 1H), 2.22-2.11 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 185.7, 178.6, 146.8, 134.6, 134.1, 132.4, 129.7, 127.0, 126.7, 125.6, 101.3, 57.6, 56.0, 39.6, 33.4. IR (thin film): v_{max} (cm⁻¹) = 3057, 3016, 2925, 2851, 1639, 1600, 1454, 1435, 1362, 1322, 1223, 1160, 1132, 1067, 1028, 834, 778, 748, 691, 664; HRMS (ESI) calcd for C₁₅H₁₄O₂ [M+H]⁺: 227.1067. Found: 227.1067.



Colorless oil. 99% yield (41.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.59-7.48 (m, 2H), 7.44-7.35 (m, 1H), 6.94 (d, *J* = 10.0 Hz, 1H), 6.47 (d, *J* = 10.4 Hz, 1H), 5.06 (s, 1H), 4.80-4.65 (m, 3H), 4.22 (d, *J* = 8.8 Hz, 1H), 4.14 (d, *J* = 8.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.8, 152.1, 149.8, 145.4, 133.0, 131.0, 127.4, 127.3, 127.0, 126.4, 108.5, 80.0, 72.1, 53.1. IR (thin film): v_{max} (cm⁻¹) = 3068, 3060, 2976, 2853, 1659, 1599, 1455, 1390, 1298, 1157, 1070, 928, 840, 764; HRMS (ESI) calcd for C₁₄H₁₃O₂ [M+H]⁺: 213.0910. Found: 213.0911.



White solid, M.P. = 98-99 °C. 86% yield (33.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.57-7.50 (m, 1H), 7.49-.40 (m, 1H), 6.58 (s, 1H), 6.45 (dt, J = 9.2, 2.0 Hz, 1H), 6.18-6.09 (m, 1H), 5.30 (s, 1H), 3.14 (t, J = 8.8 Hz, 2H), 2.51-2.42 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 132.5, 131.1, 128.8, 128.0, 126.5, 124.2, 123.9, 123.2, 122.6, 122.0, 108.2, 23.3, 22.0. IR (thin film): v_{max} (cm⁻¹) = 3338, 3064, 3030, 2925, 1951, 1703, 1594, 1519, 1388, 1359, 1310, 1267, 1220, 1064, 852, 764, 710, 637, 613; HRMS (EI) calcd for C₁₄H₁₂O [M+H]⁺: 196.0888. Found: 196.0886.

Gram-scale reaction of 1g and transformations of 2f



A flame-dried Schlenk tube was cooled down to room temperature under argon. To this tube were added Ph₃PAuOMs (1.1 mg, 0.0002 mmol, 0.05 mol%), 1-naphthol derivatives **1g** (1.1 g, 4 mmol, 1.0 equiv.), and DCM (2.0 mL). Then the reaction mixture was stirred at room temperature in the dark. After completion (monitored by TLC), the crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired product **2g** (1.1 g, 99% yield).



A flame-dried Schlenk tube was cooled down to room temperature under argon. To this tube were added $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol, 5 mol%), CuI (1.9 mg, 0.01 mmol, 5 mol%), **2f** (0.2 mmol, 1.0 equiv.), NEt₃ (2.0 mL), and ethynyltrimethylsilane (29.5 mg, 0.2 mmol, 1.0 equiv.). Then the reaction mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was filtrated through celite and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired product **3f**.



Yellow oil. 99% yield (58.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.55 (td, *J* = 7.6, 1.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 10.4 Hz, 1H), 6.44 (d, *J* = 10.0 Hz, 1H), 6.35 (t, *J* = 2.4 Hz, 1H), 2.87-2.72 (m, 2H), 2.50-2.35 (m, 2H), -0.10 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 151.9, 147.0, 138.9 132.7, 131.6, 130.0, 127.5, 127.2, 127.1, 126.1, 99.0, 98.4, 57.3, 38.6, 32.4, -0.4. IR (thin film): v_{max} (cm⁻¹) = 3064, 3034, 2959, 2899, 2851, 2147, 1662, 1600, 1456, 1389, 1300, 1249, 1155, 1128, 1065, 1027, 956, 838, 762, 702, 644, 625; HRMS (ESI) calcd for C₁₉H₂₁OSi [M+H]⁺: 293.1356. Found: 293.1358.



A flame-dried Schlenk tube was cooled down to room temperature under argon. To this tube were added **2f** (128.9 mg, 0.4 mmol, 1.0 equiv.), phenyl vinyl sulfone (672.8 mg, 4 mmol, 10.0 equiv.), and benzene (2.0 mL). Then the reaction mixture was stirred at 80°C. A solution of Bu₃SnH (232.8 mg, 0.8 mmol, 2.0 equiv.) and AIBN (13.1 mg, 0.08 mmol, 0.2 equiv.) in benzene (4 mL) was added into the reaction mixture through syringe pump over 6 h. After completion (monitored by TLC), benzene was removed under reduced pressure and the residue was diluted by Et₂O (10 mL) and saturated KF solution (10 mL). The mixture was stirred vigorously at room

temperature for 2 h.

The mixture was filtrated through filter paper and extracted with Et_2O (10 mL x 3). The combined Et_2O extract was washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford the desired product **4f**.

White solid, M.P. = 161-162 °C. 55% yield (80.1 mg). ¹H NMR (600 MHz, CDCl₃) δ 8.00 (dd, J = 7.8, 1.2 Hz, 1H), 7.85 (dd, J = 7.8, 1.8 Hz, 2H), 7.67-7.62 (m, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.51 (td, J = 7.8, 1.2 Hz, 1H), 7.32-7.28 (m, 1H), 7.25 (d, J = 8.4 Hz, 1H), 5.64 (s, 1H), 3.50-3.44 (m, 1H), 2.98-2.90 (m, 1H), 2.89-2.86 (m, 1H), 2.85 (t, J = 5.4 Hz, 1H), 2.81-2.75 (m, 2H), 2.73 (dd, J = 16.8, 3.6 Hz, 1H), 2.34-2.26 (m, 1H), 2.14-2.02 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 195.7, 149.5, 146.2, 138.6, 134.8, 133.9, 130.7, 129.4, 128.4, 127.2, 127.1, 126.8, 122.7, 67.9, 62.0, 45.8, 38.0, 37.4, 36.6, 25.9. IR (thin film): v_{max} (cm⁻¹) = 3063, 2924, 2850, 1680, 1598, 1478, 1449, 1410, 1358, 1335, 1289, 1258, 1217, 1177, 1141, 1084, 1020, 996, 972, 941, 923, 889, 841, 796, 762, 744, 725, 688, 667; HRMS (ESI) calcd for C₂₂H₂₄NO₃S [M+NH₄]⁺: 382.1471. Found: 382.1474.

Gold-catalyzed asymmetric dearomatization of naphthols and HPLC chromatographs

Optimization of reaction conditions CPA screening



Ligand Screening



Entry	Ligand	Time	Isolated Yield (%)	ee (%)
1	PPh ₃	7 d	70	70
2	$(4-CF_{3}C_{6}H_{4})_{3}P$	7 d	72	85
3	IPr	4d	58	9
4	(2-furyl) ₃ P	4.5 d	49	62
5	$(4-OMeC_6H_4)_3P$	4.5 d	65	81
6	$(3,5-(CF_3)_2C_6H_3)_3P$	11 d	22	64
7	JohnPhos	1.5 d	76	36
		S30		

8	$(2-MeC_{6}H_{4})_{3}P$	5 d	22	57
9	SPhos	4d	59	36
10	$(4-FC_{6}H_{4})_{3}P$	5.5d	41	81
11	$(C_{6}F_{5})_{3}P$	6d	Trace	
12	$(4-\text{MeC}_6\text{H}_4)_3\text{P}$	5d	61	75

Solvent Screening



Entry	Solvent	Time	Isolated Yield (%)	ee (%)
1	toluene	7 d	72	85
2	DCM	41h	82	63
3	THF	4d	trace	
4	MeOH	16h	12	
5	o-xylene	7 d	72	79
6	PhF	7 d	83	60

Concentration Screening



Entry	Concentration	Time	Yield (%)	ee (%)
1	0.1M	7 d	66	83
2	0.2M	108 h	88	86
3	0.4M	84 h	81	88
4	0.8M	43 h	84	89
5	1.6M	24 h	77	87

Additive Screening

	OH 1a	(4-CF ₃ C ₆ (S)-TRIF	H ₄) ₃ PAuCl (5 mol%) P-CPA-Ag (5 mol%) toluene, r.t.		
Entry	Additives	Time	Yield (%)	ee (%)	Note
1	none	43h	84	89	
2	3A MS	44.5 h	69	91	25 mg
3	4A MS	44.5 h	71	91	25 mg
4	5A MS	44.5 h	74	91	25 mg
5	HOAc	44.5 h	77	85	5 mol%
6	CF ₃ CF ₂ OH	44.5 h	75	88	5 mol%
7	5A MS	49.5 h	67	92	25 mg
8	5A MS	49.5 h	72	92	50 mg
9	5A MS	49.5 h	70	92	100 mg
10	5A MS	70 h	69	92	50 mg

Gold-catalyzed asymmetric dearomatization of naphthols



To a flame-dried Schlenk tube at room temperature under argon were added $(4-CF_3C_6H_4)_3PAuCl (13.8 mg, 0.02 mmol, 5 mol%)$, 1-naphthol derivatives **1a** (78.5 mg, 0.4 mmol, 1.0 equiv.), and toluene (0.5 mL). Then (*S*)-TRIP-CPA-Ag (17.2 mg, 0.02 mmol, 5 mol%) was added last. Then the reaction mixture was stirred at room temperature in the dark. After completion (monitored by TLC), the reaction mixture

was quenched by Bu_4NCl (1M in toluene, 0.1 mL) and loaded on the silica column. The crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired product **2a**.



Colorless oil, 85% yield (66.9 mg), 90% ee [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (major) = 14.27 min, t (minor) = 16.13 min]; $[\alpha]_{D}^{20} = -55.9$ (c = 1.0, CHCl₃).







2	16.130	542528	5.00	28526

Copies of NMR spectra



S35
















































S58













































































































































wwt-4-96h

 $\begin{array}{c} & 8.171 \\ & 8.152 \\ & 7.537 \\ & 7.533 \\ & 7.530 \\ & 7.530 \\ & 7.530 \\ & 7.530 \\ & 7.406 \\ & 6.954 \\ & 6.954 \\ & 6.954 \\ & 6.454 \end{array}$

 $\begin{smallmatrix} 5. & 057 \\ -4. & 769 \\ -4. & 733 \\ -4. & 730 \\ -4. & 705 \\ -4. & 697 \\ -4. & 679 \\ -4. & 674 \\ -4. & 235 \\ -4. & 213 \\ -4. & 213 \\ -4. & 124 \\ \end{smallmatrix}$

















wwt-8-43-2D

Sample Name: wwt-8-43-2D Data Collected on: OMC-NAGOO-vnmre600 Archive directory: /home/omc/vnmreys/data Sample directory: wwt-8-43-2D_20150324_01 FidFile: gCOSY_01

Pulse Sequence: gCOSY Solvent: cdcl3 Data collected on: Mar 24 2015

Temp. 25.0 C / 298.1 K Operator: omd

Relax. delay 1.000 sec Acq. time 0.249 sec Width 6188.1 Hz 2D Width 6188.1 Hz 2 repetitions 128 increments 0BSERVE H1, 599.7754542 MHz 0BSERVE H1, 599.7754542 MHz 0BSERVE H1, 599.7754542 MHz 0BATA PROCESSING Sq. sine bell 0.080 sec P1 DATA PROCESSING Sq. sine bell 0.021 sec P1 cize 4096 x 4096 Total time 5 min 11 sec











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