Supporting Information

PPh_3AuTFA catalyzed in the dearomatization of 2-naphthols with allenamides

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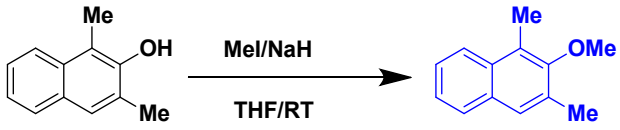
General Methods.

^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm). Monodimensional NOE experiment (400 MHz, $CDCl_3$, 25 °C) was performed by using a DPFGSE-NOE sequence, with a 50 Hz pulse and a mixing time of 1.5 s. Irradiation at the frequency of proton H^1 (5.65 ppm) showed strong positive NOE response of the H^4 frequency, confirming the *sin*-relationship. Weaker NOE effects were also observed for the equatorial H^2 and the axial H^3 protons.

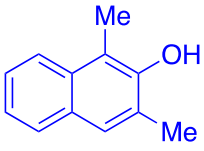
GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected. Agilent Technologies LC/MSD Trap 1100 series (nebulizer: 15.0 PSI, dry Gas: 5.0 L/min, dry Temperature: 325 °C, capillary voltage positive scan: 4000 mA, capillary voltage negative scan: 3500 mA). Preparation of β-naphthols **1**[1] and *N*-allenyl amides[2] were accomplished following the reported procedures.

Preparation of MeO-1a



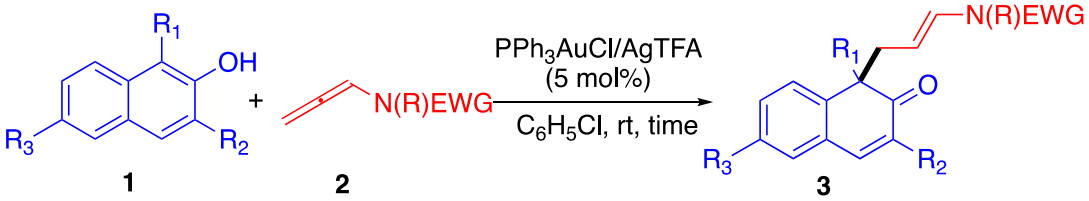
1a **MeO-1a**

An oven-dried two-necked flask was charged with **1a** (80 mg, 0.5 mmol) and NaH (37 mg, 2.0 equiv) in a sequence and left stirring for 30 min at 0 ℃. MeI (85.6 mg, 1.2 equiv) was then added and the mixture kept stirring until **1a** was completely converted (monitored by TLC). Then, water was added and the mixture extracted with ethyl acetate. At last, organic phase was collected and dried with anhydrous sodium sulfate. After removing the organic solvent under vaccun, the reaction crude was transferred to silica gel column chromatography (*c*Hex:EtOAc = 40:1) to afford compounds **MeO-1a**.



MeO-**1a**. Colorless oil, yield = 75% (70 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ = δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.48 – 7.39 (m, 1H), 3.81 (s, 3H), 2.63 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.14, 132.77, 131.20, 131.04, 127.69, 127.51, 125.20, 124.68, 124.61, 123.93, 60.65, 17.19, 11.51. GC-MS (m/z): 186. Anal. Calc. for ($C_{13}H_{14}O$: 186.25): C, 83.83; H, 7.58; found: C, 83.65, H, 7.41.

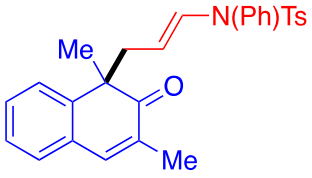
General procedure for gold-catalyzed dearomatization of 2-naphthols with *N*-allenyl amides.



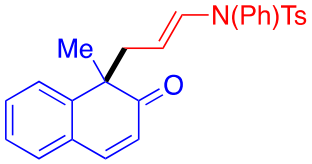
1 **2** **3**

An oven-dried two-necked flask was charged with anhydrous chlorobenzene (1 ml), Ph_3PAuCl (1.2 mg, 5 mol%) and AgTFA (0.6 mg, 5 mol%). After stirring for 15 min, substrate **1** (0.05 mmol) and **2** (0.1 mmol) were added under dark atmosphere. Then, the reaction was kept stirring at room temperature until **1** was completely consumed (TLC). At last, the solution was directly transferred into silica gel column chromatography (*c*Hex:EtOAc = 40:1 → 15:1) to afford compounds **3**.

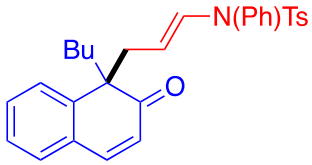
1 mmol (1a) scale reaction. An oven dried two-necked flask was charged with anhydrous chlorobenzene (15 ml), Ph_3PAuCl (12.3 mg, 2.5 mol%) and AgTFA (5.5 mg, 2.5 mol%). After stirring for 15 min, substrate **1a** (1 mmol) and **2** (1.5 mmol) were added under dark atmosphere. Then, the reaction was kept stirring at room temperature until **1a** was completely consumed (TLC). At last, the solution was directly transferred into silica gel column chromatography (*c*Hex:EtOAc = 40:1 → 15:1) to afford compounds **3aa** (0.88 mmol, 403 mg, 88%).



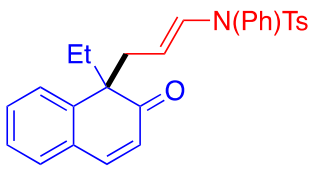
(+/-)-**3aa**. Colorless oil, yield = 98% (22 mg, 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.18 (m, 10H), 7.13 (d, *J* = 8 Hz, 1H), 7.08 (s, 1H), 6.67 – 6.65 (m, 2H), 6.58 (d, *J* = 12.0 Hz, 1H), 3.85-3.78 (m, 1H), 2.63 (dd, *J* = 12, 6.4 Hz, 1H), 2.42 (s, 3H), 2.35 (dd, *J* = 8.4, 4.8 Hz, 1H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.39 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.90, 145.09, 143.69, 141.68, 136.65, 135.98, 132.56, 131.15, 130.33, 130.11(2C), 129.61(2C), 129.23(2C), 128.95, 128.80, 128.37, 127.50(2C), 126.75, 126.56, 106.73, 51.85, 45.04, 25.53, 21.74, 15.76. LC-MS (m/z): 481. Anal. Calc. for ($C_{28}H_{27}NO_3S$: 457.59): C, 73.50; H, 5.95; found: C, 73.66, H, 6.05.



(+/-)-**3ba**. Colorless oil, yield = 95% (21 mg, 2 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.38 – 7.29 (m, 4H), 7.26 – 7.16 (m, 8H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 6.4 Hz, 1H), 3.90 – 3.83 (m, 1H), 2.67 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.42 (s, 3H), 2.37 (dd, *J* = 8.0, 3.2 Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.91, 145.78, 145.03, 143.71, 136.60, 135.94, 131.53, 130.10, 130.06(2C), 129.60(2C), 129.34, 129.27(2C), 128.86, 127.54(2C), 126.88, 126.84, 125.24, 121.87, 106.59, 52.24, 44.42, 25.63, 21.7. LC-MS (m/z): 288, 155. Anal. Calc. for ($C_{27}H_{25}NO_3S$: 443.56): C, 73.11; H, 5.68; found: C, 73.00, H, 5.89.

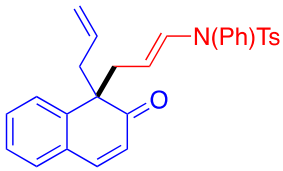


(+/-)-**3ca**. Colorless oil, yield = 95% (23 mg, 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.36 (m, 1H), 7.32-7.29 (m, 3H), 7.24 – 7.14 (m, 8H), 6.60 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 3.6 Hz, 1H), 5.93 (d, *J* = 10.0 Hz, 1H), 3.85-3.37 (m, 1H), 2.68 (dd, *J* = 10, 7.2 Hz, 1H), 2.42 (s, 2H), 2.35 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.16 (td, *J* = 12.4, 8.8 Hz, 1H), 1.76 (td, *J* = 12.4, 4.4 Hz, 1H), 1.41 (s, 3H), 1.55-0.98 (m, 2H), 0.87 – 0.73 (m, 2H), 0.68 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.20, 145.19, 144.79, 143.65, 136.63, 136.00, 131.37, 131.05, 130.18, 130.05(2C), 129.58(2C), 129.27, 129.21(2C), 128.80, 127.55(2C), 126.76, 126.71, 126.20, 106.32, 56.91, 45.07, 41.38, 27.07, 23.11, 21.75, 13.86. LC-MS (m/z): 485.6. Anal. Calc. for ($C_{30}H_{31}NO_3S$: 485.64): C, 74.20; H, 6.43; found: C, 74.01, H, 6.21.

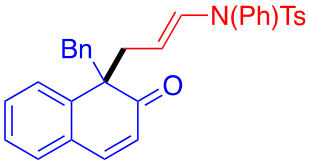


(+/-)-**3da** Colorless oil, yield = 92% (21 mg 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.36 (m, 1H), 7.31–7.28 (dd, *J* = 7.6, 4.7 Hz, 3H), 7.23

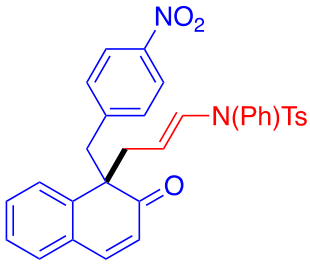
– 7.14 (m, 7H), 6.62 – 6.59 (m, 3H), 5.95 (d, *J* = 10.0 Hz, 1H), 3.86 – 3.78 (m, 1H), 2.69 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.42 (s, 3H), 2.36 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.24 – 2.15 (m, 1H), 1.85 – 1.76 (m, 1H), 0.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.24, 145.26, 144.39, 143.65, 136.61, 135.95, 131.35, 130.18, 130.03(2C), 129.58(2C), 129.29, 129.22(2C), 128.80, 127.53(2C), 126.79, 126.75, 126.27, 121.88, 106.42, 57.59, 44.65, 34.48, 21.75, 9.19. LC-MS (m/z): 480.5. Anal. Calc. for ($C_{28}H_{27}NO_3S$: 457.59): C, 73.50; H, 5.95; found: C, 73.21, H, 5.69.



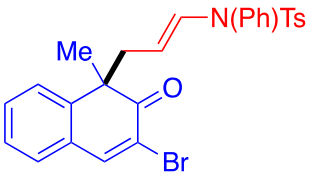
(+/-)-**3ea**. Colorless oil, yield = 68% (16 mg, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.37 (m, 1H), 7.33 – 7.30 (m, 3H), 7.24 – 7.14 (m, 8H), 6.65 – 6.59 (m, 3H), 5.93 (d, *J* = 10.0 Hz, 1H), 5.23 – 5.13 (m, 1H), 4.81 – 4.70 (m, 2H), 3.86-3.78 (m, 1H), 2.87 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.73 (dd, *J* = 13.2, 7.3 Hz, 1H), 2.53 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.42 (s, 3H), 2.42-2.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.26, 145.22, 143.93, 143.69, 136.58, 135.93, 132.81, 131.62, 130.10, 130.02(2C), 129.59(2C), 129.38, 129.24(2C), 128.84, 127.54(2C), 127.15, 126.88, 126.00, 121.90, 118.11, 106.07, 56.66, 45.35, 43.92, 21.76. LC-MS (m/z): 492. Anal. Calc. for ($C_{29}H_{27}NO_3S$: 469.60): C, 74.17; H, 5.80; found: C, 74.25, H, 5.45.



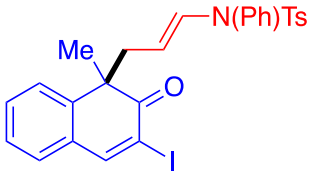
(+/-)-**3fa**. Colorless oil, yield = 77% (20 mg, 5 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.0 Hz, 1H), 7.45-7.39 (m, 2H), 7.30-7.03 (m, 10H), 6.98–6.91 (m, 3H), 6.66-6.70 (d, *J* = 16 Hz, 1H), 6.57 (t, *J* = 8.0 Hz, 3H), 5.77 (d, *J* = 10.0 Hz, 1H), 3.87 – 3.79 (m, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 3.06 (d, *J* = 12.8 Hz, 1H), 2.96 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.58 (dd, *J* = 13.2, 8.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.35, 145.06, 143.64, 136.59, 136.42, 135.88, 131.71, 131.12, 129.94(2C), 129.85, 129.64(2C), 129.56(2C), 129.32, 129.19(2C), 128.77, 127.71(2C), 127.64, 127.51(2C), 126.89, 126.37, 126.02, 121.88, 106.33, 57.93, 48.04, 43.33, 21.73. LC-MS (m/z): 542.2. Anal. Calc. for ($C_{33}H_{29}NO_3S$: 519.66): C, 76.27; H, 5.63; found: C, 76.12, H, 5.35.



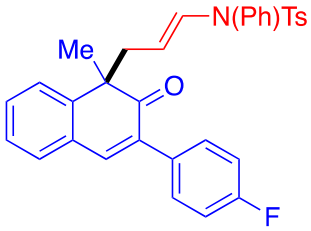
(+/-)-**3ga**. Yellow solid, yield = 62% (18 mg, 3 h). Mp = 78-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.8 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.30 – 7.14 (m, 9H), 6.99 (d, *J* = 9.6 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 13.6 Hz, 1H), 6.57-6.55 (m, 2H), 5.77 (d, *J* = 8.0 Hz, 1H), 3.84-3.76 (m, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.14 (d, *J* = 13.2 Hz, 1H), 2.94 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.60 (dd, *J* = 13.2, 8.4 Hz, 1H), 2.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.60, 146.69, 145.43, 144.41, 143.79, 142.93, 136.45, 135.86, 132.14, 131.03, 130.38(2C), 130.25, 129.96(2C), 129.69, 129.60(2C), 129.27(2C), 128.90, 127.53(2C), 127.44, 127.38, 126.03, 122.96(2C), 105.23, 57.72, 47.03, 44.17, 21.75. LC-MS (m/z): 587. Anal. Calc. for ($C_{33}H_{28}N_2O_5S$: 564.66): C, 70.20; H, 5.00; found: C, 70.41, H, 5.21.



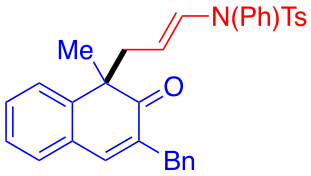
(+/-)-**3ha**. Colorless oil, yield = 95% (25 mg, 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 -7.16 (m, 11H), 6.65 (d, *J* = 6.8, 2H), 6.63 (d, *J* = 5.6, 1H), 5.94 (d, *J* = 9.6 Hz, 1H), 3.90-3.83 (m, 1H), 2.67-2.65 (m, 1H), 2.42 (s, 3H), 2.42-2.40 (m, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.90, 145.78, 145.02, 143.71, 136.61, 135.95, 131.53, 130.09, 130.06(2C), 129.59(2C), 129.34, 129.26(2C), 128.85, 127.54(2C), 126.87, 126.83, 125.24, 121.87, 106.60, 52.24, 44.41, 25.63, 21.75. LC-MS (m/z): 546. Anal. Calc. for ($C_{27}H_{24}BrNO_3S$: 522.46): C, 62.07; H, 4.63; found: C, 61.96, H, 4.51.



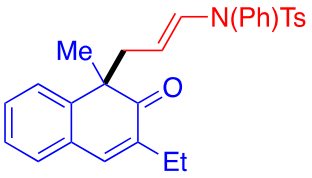
(+/-)-**3ia**. Light yellow oil, yield = 45% (13 mg, 15 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.40 (td, *J* = 8.0, 1.6 Hz, 1H), 7.35-7.20 (m, 9H), 7.3 (d, *J* =7.6 Hz, 1H), 6.71 (dd, *J* = 8.4, 1.6 Hz, 2H), 6.61 (d, *J* = 14.0 Hz, 1H), 3.82-3.75 (m, 1H), 2.63 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.42 (s, 3H), 2.35 (dd, *J* = 13.2, 8.0 Hz, 1H), 1.46 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.32, 154.22, 145.60, 143.78, 136.47, 135.87, 131.82, 131.14, 130.68, 130.14(2C), 129.73(2C), 129.44(2C), 128.95, 128.75, 127.56(2C), 127.15, 126.86, 105.48, 101.93, 53.33, 45.81, 25.84, 21.79. LC-MS (m/z): 592. Anal. Calc. for ($C_{27}H_{24}INO_3S$: 569.46): C, 56.95; H, 4.25; found: C, 56.70, H, 4.31.



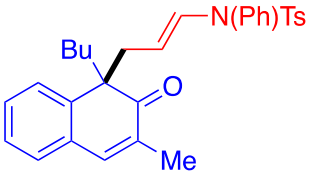
(+/-)-**3ja**. Light yellow oil, yield = 40% (11 mg, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 – 7.47 (m, 1H), 7.38 – 7.36 (m, 1H), 7.34 – 7.22 (m, 9H), 7.12- 7.17 (m, 4H), 7.01 (t, *J* = 8.8 Hz, 2H), 6.67 – 6.63 (m, 3H), 3.97 – 3.90 (m, 1H), 2.70 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.40 (s, 3H), 2.03 – 1.98 (m, 1H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.23, 163.98, 145.40, 143.74, 142.47, 136.58, 135.98, 134.42, 131.51, 130.49(d, $^{1}J_{CF}$=8.0 Hz, 1C), 130.22, 130.11(2C), 129.97, 129.88, 129.61(2C), 129.56, 129.54, 129.34(2C), 128.83, 127.47(2C), 126.84 (d, $^{2}J_{CF}$=43 Hz, 2C), 115.16(d, $^{3}J_{CF}$ =22 Hz, 2C), 106.35, 52.83, 45.26, 25.12, 21.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.87 – -113.93 (m, 1 F). LC-MS (m/z): 560. Anal. Calc. for ($C_{33}H_{28}FNO_3S$: 537.65): C, 73.72; H, 5.25; found: C, 73.62, H, 5.11.



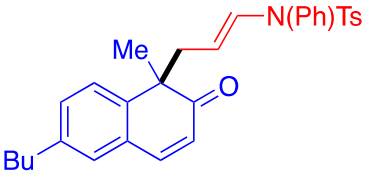
(+/-)-**3ka**. Colorless oil, yield =72% (19 mg, 6 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 – 7.51 (m, 1H), 7.48 – 7.441 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.14 (m, 10H), 7.11 – 7.04 (m, 4H), 6.83 (s, 1H), 6.66 – 6.62 (m, 3H), 3.85 – 3.77 (m, 1H), 3.51 (dd, *J* = 72.0, 16.0 Hz, 2H), 2.64 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.38 (s, 3H), 1.39 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.03, 144.96, 143.79, 141.88, 139.02, 136.69, 135.90, 135.89, 134.55, 134.42, 131.41(2C), 130.07(2C), 129.64(2C), 129.34(2C), 129.26(2C), 129.19, 128.92, 128.81, 128.64(2C), 127.53(2C), 126.74, 126.53, 126.41, 106.70, 52.08, 44.81, 35.22, 25.52, 21.72. LC-MS (m/z): 556.2. Anal. Calc. for ($C_{34}H_{31}NO_3S$: 533.69): C, 76.52; H, 5.86; found: C, 76.31, H, 5.65.



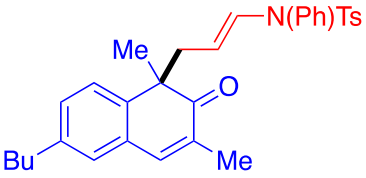
(+/-)-**3la**. Colorless oil, yield = 87% (21 mg, 4 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.15 (m, 11H), 7.02 (s, 1H), 6.67 – 6.64 (m, 2H), 6.58 (d, *J* = 12 Hz, 1H), 3.86-3.78 (m, 1H), 2.66-2.60 (m, 1H), 2.42 (s, 3H), 2.35 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.26-2.15 (m, 2H), 1.39 (s, 3H), 0.95 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.45, 144.92, 143.68, 139.95, 137.91, 136.64, 135.97, 131.20, 130.38, 130.11(2C), 129.60(2C), 129.24(2C), 128.92, 128.81, 128.57, 127.50(2C), 126.75, 126.50, 106.66, 51.87, 45.04, 25.43, 22.27, 21.74, 12.60. LC-MS (m/z): 494.2. Anal. Calc. for ($C_{29}H_{29}NO_3S$: 471.62): C, 73.86; H, 6.20; found: C, 73.70, H, 6.09.



(+/-)-**3ma**. Colorless oil, yield = 94% (24 mg, 6 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.34 – 7.11 (m, 11H), 7.06 (s, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 14 Hz, 1H), 3.78-3.71 (m, 1H), 2.63 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.42 (s, 3H), 2.34 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.20 – 2.13 (m, 1H), 1.80 – 1.72 (m, 1H), 1.75 (s, 3H), 1.13-1.01 (m, 2H), 0.76 – 0.61 (m, 1H), 0.67 (t, J=7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.07, 204.10, 144.01, 143.63, 141.98, 136.63, 135.95, 133.32, 131.53, 130.97, 130.07(2C), 129.59(2C), 129.17(2C), 129.04, 128.74, 128.31, 127.46(2C), 126.59, 126.43, 106.48, 56.50, 45.45, 41.25, 31.06, 23.10, 21.73, 15.58, 13.87. LC-MS (m/z): 522.6 Anal. Calc. for ($C_{31}H_{33}NO_3S$: 499.67): C, 74.52; H, 6.66; found: C, 74.27, H, 6.35.

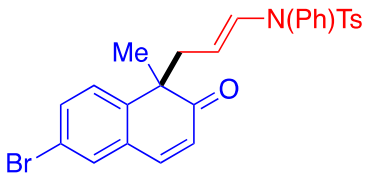


(+/-)-**3na**. Colorless oil, yield = 92% (22 mg, 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.0 Hz, 2H), 7.22 – 7.13 (m, 8H), 7.02 (m, 1H), 6.68 – 6.64 (m, 3H), 5.92 (d, J = 9.6 Hz, 1H), 3.89-3.82 (m, 1H), 2.67-2.61 (m, 1H), 2.59 (t, J= 8.0 Hz 2H), 2.42 (s, 3H), 2.35 (dd, J = 11.6, 7.6 Hz, 1H), 1.61 – 1.54 (m, 2H), 1.37 (s, 3H), 1.37 – 1.30 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.23, 145.29, 143.71, 142.93, 141.46, 136.69, 135.98, 131.36, 130.28, 130.06(2C), 129.59, 129.57(2C), 129.25, 129.22(2C), 128.77, 127.56(2C), 126.76, 125.11, 107.07, 51.93, 44.21, 35.12, 33.58, 25.60, 22.46, 21.75, 14.09. LC-MS (m/z): 523. Anal. Calc. for ($C_{31}H_{33}NO_3S$: 499.67): C, 74.52; H, 6.66; found: C, 74.31, H, 6.41.

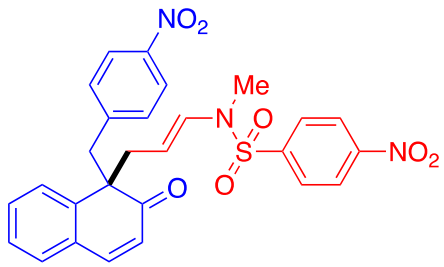


(+/-)-**3oa**. Colorless oil, yield = 86% (22 mg, 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.13 (m, 6H), 7.08 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.04 (s, 1H), 6.94 (s, 1H), 6.67 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.61(d, *J* = 14.0 Hz, 1H), 3.85-3.78 (m, 1H), 2.62 – 2.56 (m, 3H), 2.41 (s, 3H), 2.32 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.53 – 1.41 (m, 2H), 1.36 (s, 3H), 1.36-1.28 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3) δ =204.19, 143.70, 142.26, 141.94, 141.30, 136.75, 136.05, 132.35, 130.98, 130.11(2C), 130.09, 129.58(2C), 129.20(2C), 129.14, 128.72, 128.31, 127.53(2C), 126.45, 107.25,

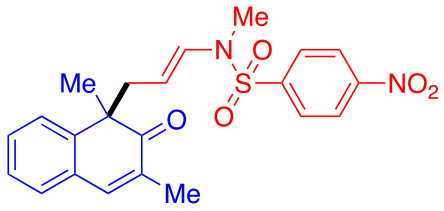
51.56, 44.84, 35.20, 33.60, 25.49, 22.46, 21.74, 15.81, 14.11. LC-MS (m/z): 536.7. Anal. Calc. for ($C_{32}H_{35}NO_3S$: 513.70): C, 74.82; H, 6.87; found: C, 74.62, H, 6.61.



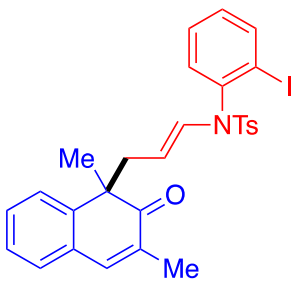
(+/-)-**3pa**. Colorless oil, yield = 44% (12 mg, 6 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.15 (m, 7H), 6.68 – 6.63 (m, 3H), 5.98 (d, *J* = 10.0 Hz, 1H), 3.88 – 3.80 (m, 1H), 3.88 – 3.80 (dd, *J*= 13.2, 6.8 Hz, 1H), 2.44 (s, 3H), 3.37 – 3.32 (dd, *J* = 13.6, 8.8 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.05, 144.53, 143.93, 143.28, 136.53, 135.80, 132.67, 131.81, 131.76, 130.04(2C), 129.67(2C), 129.36(2C), 129.00, 128.68, 127.48(2C), 126.39, 121.91, 120.50, 106.08, 52.15, 44.09, 25.69, 21.80. LC-MS (m/z): 287,155, 80. Anal. Calc. for ($C_{27}H_{24}BrNO_3S$: 522.46): C, 62.07; H, 4.63; found: C, 62.21, H, 4.42.



(+/-)-**3ab**. Yellow solid, yield = 91% (24 mg, 30 h). Mp = 62-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 3.2 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 9.6 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 14.0 Hz, 1H), 5.85 (d, *J* = 10.0 Hz, 1H), 4.27-4.20 (m, 1H), 3.30 (dd, *J* = 140, 1.4 Hz, 2H), 3.15 – 3.09 (m, 1H), 2.75 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.33, 145.60, 143.65, 142.88, 142.57, 131.19, 130.44, 130.42(2C), 130.15, 130.00, 128.59, 128.21(2C), 127.77, 127.25, 126.21, 124.54, 124.43(2C), 122.97(2C), 106.36, 57.54, 48.83, 42.36, 32.32. LC-MS = 412, 136. Anal. Calc. for ($C_{27}H_{23}N_3O_7S$: 533.55): C, 60.78; H, 4.34; found: C, 60.55, H, 4.21.

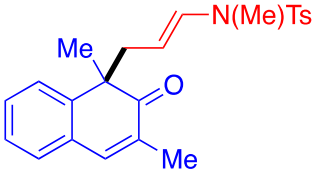


(+/-)-**3ac**. Colorless oil, *c*Hex:EtOAc = 40:1→20:1, yield = 54% (12 mg, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 – 8.22 (m, 2H), 7.65 – 7.62 (m, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 7.23-7.18 (m, 2H), 6.48 (d, *J* = 14.0 Hz, 1H), 4.33 – 4.25 (m, 1H), 2.87 (ddd, *J* = 14.0, 7.2, 1.2 Hz, 1H), 2.61 (s, 3H), 2.52 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.91 (d, *J* = 1.6 Hz, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.54, 150.13, 144.88, 143.07, 141.66, 132.61, 130.38, 129.34, 129.18, 128.84, 128.20(2C), 127.01, 126.40, 124.43(2C), 108.05, 51.88, 42.39, 32.40, 27.81, 15.93. LC-MS (m/z): 449.0. Anal. Calc. for ($C_{22}H_{22}N_2O_5S$: 426.49): C, 61.86; H, 5.20; found: C, 61.61, H, 5.01.

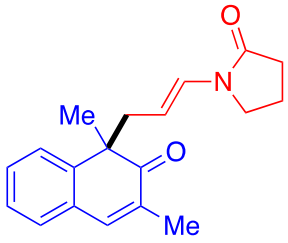


(+/-)-**3ad**. Yellow solid, cHex:EtOAc = 40:1, yield = 63% (18 mg, 10 h) Mp = 57-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 – 7.83 (m, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.30 – 7.25 (m, 5H), 7.16 –

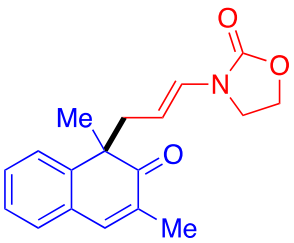
7.09 (m, 3H), 6.98 – 6.94 (m, 1H), 6.54 (dd, *J* = 36.0, 14.0 Hz, 1H), 6.36 (ddd, *J* = 59.2, 8.0, 1.6 Hz, 1H), 3.70 – 3.58 (m, 1H), 2.70 - 2.57 (m, 1H), 2.43 (d, *J* = 5.2 Hz, 3H), 2.40 – 2.33 (m, 1H), 1.78 (dd, *J* = 27.2, 0.8 Hz, 3H), 1.38 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.99 (203.79), 145.03 (144.75), 144.11 (143.91), 142.06 (141.85), 140.83 (140.73), 139.41, 136.43, 132.54 (132.22), 130.41(2C), 130.38 (130.24), 130.28 (130.15), 129.88 (129.72), 129.80(2C) (129.76(2C)), 128.89(2C), 128.68, 128.42, 127.84 (127.73), 126.76 (126.70), 126.68 (126.55), 107.67 (107.21), 102.48 (102.34), 51.77 (51.67), 44.39 (44.04), 25.88, 21.80 (21.76), 15.98 (15.74). LC-MS (m/z): 606.6. Anal. Calc. for ($C_{28}H_{26}INO_3S$: 538.48): C, 57.64; H, 4.49; found: C, 57.41, H, 4.31.



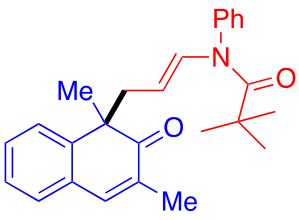
(+/-)-3ae. Colorless oil, cHex:EtOAc = 40:1→20:1, yield = 98% (19 mg, 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, J = 8.0 Hz, 2H), 7.34-7.33 (m, 2H), 7.27-7.17 (m, 5H), 6.50 (d, J = 14.0 Hz, 3H), 4.20 – 4.13 (m, 1H), 2.79 – 2.74 (m, 1H), 2.56 (s, 3H), 2.50 – 2.44 (m, 1H), 2.38 (s, 3H), 1.89 (d, J = 1.2 Hz, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 203.81, 145.05, 143.61, 141.57, 134.76, 132.64, 130.34, 130.22, 129.76(2C), 129.06, 128.67, 127.03(2C), 126.87, 126.46, 105.49, 51.88, 43.48, 32.15, 26.63 21.67, 15.91. LC-MS (m/z): 418.0. Anal. Calc. for ($C_{23}H_{25}NO_3S$: 395.51): C, 69.84; H, 6.37; found: C, 69.66, H, 6.51.



(+/-)-**3af**. Colorless oil, *c*Hex:EtOAc = 40:1→20:1, yield = 82% (12 mg, 15 h).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.32 (m, 2H), 7.25 – 7.20 (m, 3H), 6.65 (d, *J* = 14.4 Hz, 1H), 4.45-4.37 (m, 1H), 3.28 – 3.17 (m, 2H), 2.77 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.49 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.37 (t, *J* = 8.8 Hz, 2H), 2.00 – 1.92 (m, 2H), 1.96 (s, 3H), 1.43 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.95, 172.91, 145.14, 141.58, 132.56, 130.26, 129.10, 128.67, 126.90, 126.48, 125.97, 106.60, 51.91, 45.21, 43.60, 31.28, 26.08, 17.37, 16.04. LC-MS (m/z): 318.0. Anal. Calc. for ($C_{19}H_{21}NO_2$: 295.38): C, 77.26; H, 7.17; found: C, 77.01, H, 7.31.

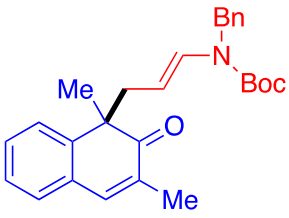


(+/-)-**3ag**. Colorless oil, *c*Hex:EtOAc = 40:1→20:1, yield = 88% (13 mg, 10 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 3.2 Hz, 2H), 7.26 – 7.21(m, 3H), 6.43 (d, *J* = 14.4 Hz, 1H), 4.32 – 4.25(m, 3H), 3.47 – 3.36 (m, 2H), 2.79 (dd, *J* = 14.0, 8.0Hz, 1H), 2.49 (dd, *J* = 10.0, 8.0 Hz, 1H), 1.97 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.84, 155.23, 145.02, 141.64, 132.57, 130.27, 129.17, 128.73, 126.98, 126.44, 126.23, 105.55, 62.09, 51.88, 43.04, 42.53, 26.42, 16.03. LC-MS (m/z): 320.2. Anal. Calc. for ($C_{18}H_{19}NO_3$: 297.35): C, 72.71; H, 6.44; found: C, 72.55, H, 6.21.



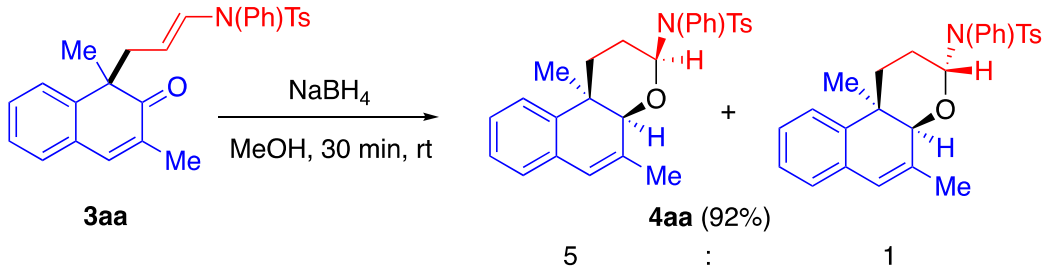
(+/-)-**3ah**. Yellow oil, yield = 54% (11 mg, 48 h).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.28 (m, 3H), 7.23 – 7.17 (m, 3H), 7.23 – 7.17 (d, *J* = 7.2 Hz,1H), 7.08 (s, 1H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.87 – 6.85 (m, 2H),

3.73 – 3.65 (m, 1H), 2.59 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.32 (dd, *J* = 12.0, 8.4 Hz, 1H), 1.83 (s, 3H), 1.39 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.13, 176.02, 145.11, 141.78, 140.32, 133.70, 132.51, 130.25(2C), 129.04(2C), 128.90, 128.30, 128.16, 126.73, 126.60, 120.08, 108.99, 51.81, 45.75, 29.13, 27.80, 24.88, 15.86. LC-MS (m/z): 410. Anal. Calc. for ($C_{26}H_{29}NO_2$: 387.52): C, 80.59; H, 7.54; found: C, 80.50, H, 7.22.



(+/-)-**3ai**. Colorless oil, yield = 92% (19 mg, 3 h). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.14 (m, 5H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 3H), 6.49 (d, *J* = 13.2 Hz, 1H), 4.44 (s, 2H), 4.12 (s, 1H), 2.59 (s, 1H), 2.35 (s, 1H), 1.46 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.28, 201.33, 153.21, 145.03, 141.77, 132.31, 130.37, 129.42, 128.72, 128.51(2C), 126.76, 126.53(2C), 126.47, 103.82, 103.42, 81.36, 51.81, 39.85, 33.91, 29.83, 28.55, 28.35, 25.25. LC-MS (m/z): 440.2. Anal. Calc. for ($C_{27}H_{31}NO_3$: 417.55): C, 77.67; H, 7.48; found: C, 77.51, H, 7.37.

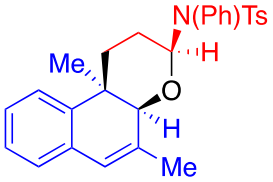
Synthesis of the *1H*-benzochromene 4aa:



3aa **4aa** (92%)

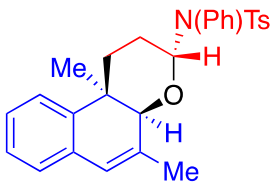
5 : 1

A one-necked flash was charged with reagent grade methanol (2 ml), racemic **3aa** (0.1 mmol) and $NaBH_4$ (0.15 mmol) in a sequence. The reaction was stirred at rt for 0.5 h at rt. The solvent was removed under vacuum, then water was added and the product extract three times with AcOEt. After dryness with Na_2SO_4 the volatiles were removed under vacuum. ^{1}H-NMR spectrum was collected on the crude mixture (*dr* = 5:1). Finally, the product was purified by flash chromatography (combined yield = 92%, 42.3 mg).



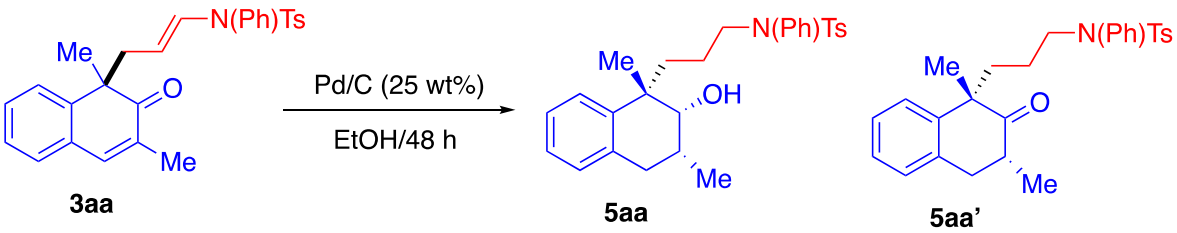
4aa-(major isomer), colorless oil, cHex:EtOAc = 40:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, J = 8.4 Hz, 2H), 7.09 – 6.83 (m, 10H), 6.25 (d, J = 1.2 Hz, 1H), 5.63 (dd, J = 11.2, 2.4 Hz, 1H), 3.67 (s, 1H), 2.44 (dt, J = 14.4, 3.2 Hz, 1H), 2.35 (s, 3H), 1.99 (d, J = 3.2 Hz, 3H), 1.72 (td, J = 13.2, 3.2 Hz, 1H), 1.44 – 1.41 (m, 4H), 1.28 – 1.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.06, 138.78, 136.97, 136.07, 133.43, 133.19, 131.01(2C), 128.80(2C), 128.51(2C), 128.07(2C), 128.00, 127.22, 126.90, 126.05, 125.91, 123.92, 85.87, 82.57, 37.07, 32.53, 26.88, 26.58, 22.15,

21.67. LC-MS (m/z): 482.0. Anal. Calc. for ($C_{28}H_{29}NO_3S$: 459.60): C, 73.17; H, 6.36; found: C, 73.01, H, 6.29.



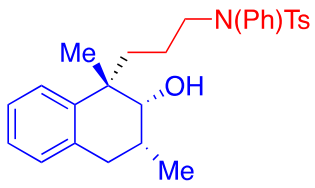
4aa-(minor isomer), colorless oil, cHex:EtOAc = 40:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 8.4, 2.8 Hz, 2H), 7.35 – 7.03 (m, 10H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.34 (s, 1H), 5.71 (dd, J = 10.8, 3.2 Hz, 1H), 4.40 (s, 1H), 2.39 (s, 3H), 2.04 (s, 3H), 2.04 – 2.02 (s, 2H), 1.50 – 1.47 (m, 1H), 1.39 – 1.37 (m, 1H), 1.2 7 (s, 3H). LC-MS (m/z): 482.0.

Hydrogenation of 3aa:

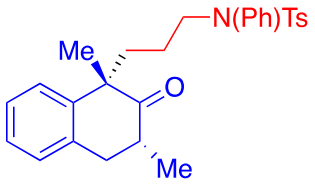


3aa **5aa** **5aa'**

An oven-dried two-necked flask was charged with ethanol (3 ml), **3aa** (27 mg, 0.06 mmol) and Pd/C (8.2 mg, 25 wt%). The flack was subjected to H_2 atmosphere (1 atm, balloon) and the reaction was stirred at room temperature for 48 h. Then, the mixture was then filtrated through celite and concentrated under reduced pressure. The residue was purified via flash-chromatography on silica gel (*c*Hex:AcOEt = 20:1) to afford compound **5aa** and **5aa'**.



5aa, colorless oil, yield = 45% (13 mg), *c*Hex:EtOAc = 40:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 3H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.08 – 7.06 (m, 3H), 7.02 (d, *J* = 7.2 Hz, 1H), 3.63 – 3.43 (m, 2H), 3.44 (s, 1H), 2.64 – 2.60 (m, 2H), 2.40 (s, 3H), 2.12 – 2.06 (m, 1H), 1.91 – 1.81 (m, 2H), 1.67 – 1.51 (m, 2H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.42, 142.91, 139.46, 135.37, 135.00, 129.49(2C), 129.12(2C), 128.98, 128.89(2C), 127.95, 127.91(2C), 126.98, 126.50, 125.74, 75.98, 51.51, 42.00, 35.34, 32.49, 28.99, 28.96, 23.11, 21.69, 18.83. LC-MS (m/z): 463. Anal. Calc. for ($C_{28}H_{33}NO_3S$: 463.63): C, 72.54; H, 7.17; found: C, 72.25, H, 7.05.



5aa', colorless oil, yield = 33% (9 mg), *c*Hex:EtOAc = 40:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.0 Hz, 2H), 7.22 – 7.16 (m, 7H), 7.13 – 7.09 (m, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.85 – 6.82 (m, 2H), 3.42 – 3.35 (m, 1H), 3.26 – 3.20 (m, 1H), 2.88 (dd, J = 15.2, 5.6 Hz, 1H), 2.74 – 2.68 (m, 1H), 2.56 (d, J = 15.2 Hz, 1H), 2.38 (s, 3H), 2.25 (ddd, J = 16.0, 11.6, 5.6 Hz, 1H), 1.68 – 1.60 (m, 1H), 1.38 (s, 3H), 1.07 (d, J = 6.4 Hz, 3H), 1.01 – 0.91 (m, 1H), 0.84 – 0.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 215.23, 143.12, 141.77, 138.75, 135.64, 135.37, 129.78, 129.35, 129.24(2C), 128.76(2C), 127.66(2C), 127.63(2C), 126.99, 126.54, 126.19, 51.56, 50.61, 40.51, 37.13, 36.89, 28.80, 23.64, 21.47, 14.33. LC-MS (m/z): 491.0 . Anal. Calc. for ($C_{28}H_{31}NO_3S$: 461.62): C, 72.85; H, 6.77; found: C, 72.61, H, 6.51.

Preparation of $Ph_3PAuTFA$[3]

An oven-dried two-necked flask was charged with anhydrous DCM (3 ml) and AuCl-SMe_2 (39.3 mg, 0.15 mmol). Then a solution of Ph_3P (44.2 mg, 0.1 5mmol) in DCM (3 ml) was added dropwise. After 1 h the solvent was removed under reduced pressure and the residue was triturate in anhydrous diethyl ether. After removing the diethyl ether under vacuum, PPh_3AuCl was collected as a white powder (59 mg, 80%).

A dry two-necked flask was charged with anhydrous DCM (3 ml) and PPh_3AuCl (59 mg, 0.12 mmol). The flask was covered with an aluminum foil when AgTFA (26.4 mg, 0.12 mmol) was added. After stirring at room temperature for 1 h, the solution was filtered through syringe PTFE filter (CHROMAFILM Xtra, 0.45 µm). The solvent was removed under reduced pressure and the crude triturate with anhydrous diethyl ether. Upon removal of the diethyl ether under vacuum, PPh_3AuTFA was collected as a white power (59 mg, 83%).

PPh_3AuTFA. White powder. ^1H NMR (400 MHz, CD_2Cl_2) δ = 7.59-7.51 (m, 15H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ = -74.31 (s, 3F). ^{31}P NMR (160 MHz, CD_2Cl_2) δ = 30.04(s).

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