

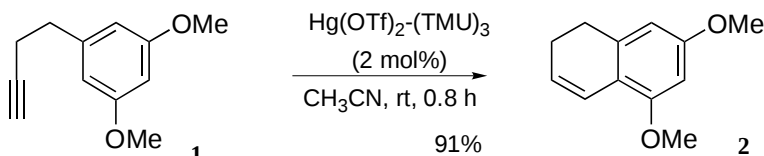
Mercuric Triflate-(TMU)₃- Catalyzed Cyclization of ω -Arylalkyne Leading to Dihydronaphthalenes

Mugio Nishizawa,* Hiroko Takao, Veejendra K. Yadav,[†] Hiroshi Imagawa, and Takumichi Sugihara

Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770-8514, Japan

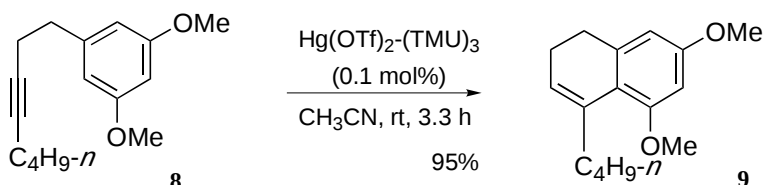
mugi@ph.bunri-u.ac.jp

General procedure: General procedure is as follows. To a stirred solution of Hg(OTf)₂-(TMU)₃ complex, prepared by mixing triflic anhydride and yellow mercuric oxide in CH₃CN at 0°C and then TMU, was added a solution of an aryl alkyne (1 mmol) in CH₃CN (total 3 mL), and the resulting mixture was stirred at the indicated temperature until all starting material was consumed. After aqueous work-up by adding aq NaHCO₃-NaCl (1:1) solution, the organic extract was dried and concentrated. Column chromatography of the crude material with hexane and ethyl acetate afforded the product.



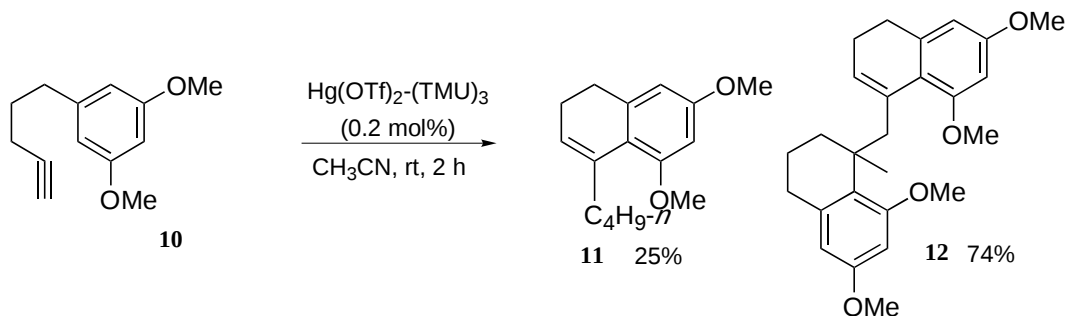
1 : IR (neat) 3292, 2931, 2839, 2117, 1608, 1207, 1161, 1068 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.00 (1 H, t, J = 2.6 Hz), 2.48 (2 H, dt, J = 2.6, 7.6 Hz), 2.80 (2 H, t, J = 7.6 Hz), 3.78 (6 H, s), 6.34 (1 H, d, J = 2.2 Hz), 6.39 (2 H, d, J = 2.2 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 20.24, 34.96, 55.01, 55.01, 68.91, 83.65, 98.01, 106.25, 106.25, 142.58, 160.56, 160.56. MS (CI) m/z 191 (M^+ +1). HR-MS (CI) calcd. for C₁₂H₁₅O₂ (M^+ +1) 191.1072, found 191.1066.

2 : IR (neat) 2833, 1627, 1605, 1577, 1489, 1464, 1577, 1149, 1107, 1052 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 2.26 (2 H, ddt, J = 1.9, 4.4, 8.2 Hz), 2.73 (2 H, t, J = 8.2 Hz), 3.80 (3 H, s), 3.80 (3 H, s), 5.89 (1 H, dt, J = 4.4, 9.6 Hz), 6.30 (2 H, br s), 6.75 (1 H, dt, J = 1.9, 9.6 Hz). ¹³C NMR (150 MHz, CDCl₃) δ 22.79, 28.46, 55.30, 55.48, 96.27, 104.73, 116.27, 121.19, 124.76, 138.04, 155.74, 159.30. MS (EI) m/z 190 (M^+). HR-MS (EI) calcd. for C₁₂H₁₄O₂ (M^+) 190.0994, found 190.0980.



8 : IR (neat) 2955, 2867, 2124, 1207, 1161, 1069 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 0.90 (3 H, t, J = 7.3 Hz), 1.33-1.48 (4 H, m), 2.15 (2 H, dt, J = 2.3, 6.9 Hz), 2.43 (2 H, dt, J = 2.3, 7.6 Hz), 2.74 (2 H, t, J = 7.6 Hz), 3.78 (6 H, s), 6.32 (1 H, t, J = 2.2 Hz), 6.38 (2 H, d, J = 2.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 13.58, 18.39, 20.82, 21.87, 31.12, 35.90, 55.09, 55.09, 79.30, 80.91, 98.03, 106.39, 106.39, 143.31, 160.61, 160.61. MS (CI) m/z 247 (M^+ +1). HR-MS (CI) calcd. for C₁₆H₂₃O₂ (M^+ +1) 247.1698, found 247.1701.

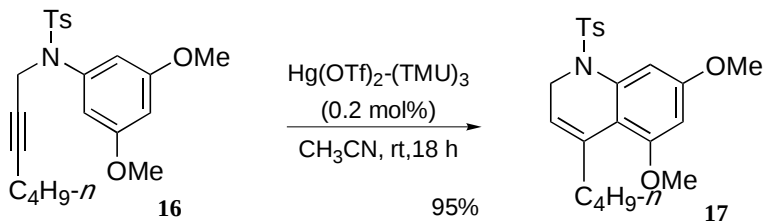
9 : IR (neat) 2933, 2856, 2834, 1603, 1573, 1463, 1158, 1110 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 0.87 (3 H, t, J = 7.1 Hz), 1.26-1.36 (4 H, m), 2.04-2.07 (2 H, m), 2.58-2.62 (4 H, m), 3.78 (3 H, s), 3.80 (3 H, s), 5.75 (1 H, tt, J = 1.1, 4.9 Hz), 6.34 (1 H, d, J = 2.5 Hz), 6.37 (1 H, d, J = 2.5 Hz). ¹³C NMR (150 MHz, CDCl₃) δ 14.06, 22.58, 22.72, 30.92, 31.63, 36.20, 55.18, 55.24, 97.15, 105.00, 117.30, 123.60, 137.41, 141.49, 157.28, 158.73. MS (CI) m/z 247 (M^+ +1). HR-MS (CI) calcd. for C₁₆H₂₃O₂ (M^+ +1) 247.1698, found 247.1702.



10 : IR (neat) 3290, 2926, 2854, 2116, 1595, 1203, 1147, 1070 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 1.61-1.89 (2 H, m), 2.00 (1 H, t, $J = 2.6$ Hz), 2.21 (2 H, dt, $J = 2.6, 7.0$ Hz), 2.68 (2 H, t, $J = 7.6$ Hz), 3.78 (6 H, s), 6.31 (1 H, t, $J = 2.2$ Hz), 6.36 (2 H, d, $J = 2.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 17.58, 29.66, 34.69, 54.85, 54.85, 68.72, 83.92, 97.58, 106.27, 106.27, 143.58, 160.53, 160.53. MS (CI) m/z 205 ($\text{M}^+ + 1$). HR-MS (CI) calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_2$ ($\text{M}^+ + 1$) 205.1228, found 205.1222.

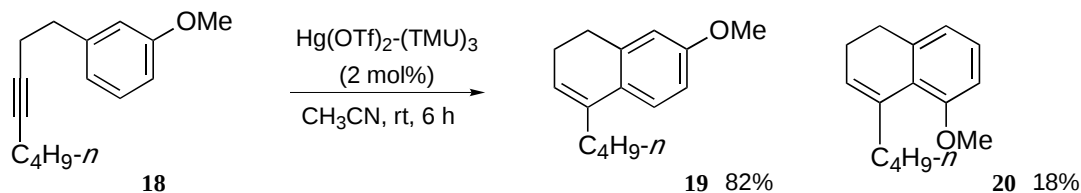
11 : IR (neat) 2935, 2833, 1604, 1232, 1204, 1158, 1108, 830, 801 cm^{-1} . ^1H NMR (600 MHz, CDCl_3) δ 2.05-2.10 (2 H, m), 2.17 (3 H, q, $J = 1.7$ Hz), 2.62 (2 H, t, $J = 7.7$ Hz), 3.77 (3 H, s), 3.80 (3 H, s), 5.70 (1 H, tq, $J = 1.7, 4.7$ Hz), 6.34 (1 H, d, $J = 2.5$ Hz), 6.36 (1 H, d, $J = 2.5$ Hz). ^{13}C NMR (150 MHz, CDCl_3) δ 22.80, 23.18, 30.56, 55.23, 55.42, 97.40, 104.98, 118.31, 123.96, 132.50, 140.83, 157.77, 158.83. MS (CI) m/z 204 (M^+). HR-MS (CI) calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ (M^+) 204.1150, found 204.1144.

12 : IR (neat) 2948, 1610, 1466, 1205, 1161, 1049, 953, 909, 829, 733 cm^{-1} . ^1H NMR (600 MHz, CDCl_3) δ 1.19-1.25 (1 H, m), 1.21 (3 H, s), 1.47-1.53 (1 H, m), 1.62-1.70 (2 H, m), 1.91-2.00 (2 H, m), 2.38-2.43 (1 H, m), 2.46-2.51 (1 H, m), 2.59 (2 H, ddt, $J = 6.9, 16.2, 30.6$ Hz), 3.05 (1 H, d, $J = 13.5$ Hz), 3.54 (1 H, d, $J = 13.5$ Hz), 3.77 (3 H, s), 3.79 (3 H, s), 3.80 (3 H, s), 3.81 (3 H, s), 5.72 (1 H, t, $J = 4.9$ Hz), 6.19 (1 H, d, $J = 2.8$ Hz), 6.30 (1 H, d, $J = 2.8$ Hz), 6.32 (1 H, d, $J = 2.5$ Hz), 6.35 (1 H, d, $J = 2.5$ Hz). ^{13}C NMR (150 MHz, CDCl_3) δ 19.38, 23.20, 26.55, 31.10, 32.68, 38.05, 38.23, 42.12, 54.97, 55.08, 55.08, 55.16, 97.03, 97.41, 104.39, 104.83, 119.72, 126.75, 128.21, 134.74, 139.80, 141.22, 157.31, 157.60, 158.39, 159.98. MS (CI) m/z 408 (M^+). HR-MS (CI) calcd. for $\text{C}_{26}\text{H}_{32}\text{O}_4$ (M^+) 408.2301, found 408.2324.



16 : IR (neat) 3005, 2955, 2867, 2236, 1591, 1462, 1426, 1351, 1202, 1153, 1064 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.83 (3 H, t, $J = 6.9$ Hz), 1.17-1.35 (4 H, m), 2.01 (2 H, tt, $J = 2.2, 6.9$ Hz), 2.41 (3 H, s), 3.71 (6 H, s), 4.38 (2 H, t, $J = 2.2$ Hz), 6.39 (1 H, t, $J = 2.2$ Hz), 6.44 (2 H, d, $J = 2.2$ Hz), 7.23 (2 H, d, $J = 8.2$ Hz), 7.61 (2 H, d, $J = 8.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 13.38, 18.12, 21.35, 21.63, 30.23, 41.54, 55.16, 55.16, 74.09, 86.06, 100.07, 106.14, 106.14, 127.95, 127.95, 128.91, 128.91, 135.80, 141.30, 143.29, 160.35, 160.35. MS (CI) m/z 402 ($\text{M}^+ + 1$). HR-MS (CI) calcd. for $\text{C}_{22}\text{H}_{28}\text{NO}_4\text{S}$ ($\text{M}^+ + 1$) 402.1739, found 402.1744.

17 : IR (neat) 2955, 1606, 1465, 1165, 1051 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.50-0.60 (2 H, m), 0.78 (3 H, t, $J = 7.4$ Hz), 1.08 (2 H, tt, $J = 7.4, 7.4$ Hz), 2.12-2.18 (2 H, m), 2.33 (3 H, s), 3.73 (3 H, s), 3.87 (3 H, s), 4.22 (2 H, d, $J = 5.0$ Hz), 5.23 (1 H, tt, $J = 1.4, 5.0$ Hz), 6.35 (1 H, d, $J = 2.5$ Hz), 7.03 (1 H, d, $J = 2.5$ Hz), 7.09 (2 H, d, $J = 8.5$ Hz), 7.19 (2 H, d, $J = 8.5$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 13.94, 21.27, 22.74, 30.70, 34.44, 44.97, 55.16, 55.40, 97.74, 103.28, 113.79, 116.98, 127.23, 127.23, 128.97, 128.97, 137.06, 137.18, 138.29, 142.94, 157.05, 159.00. MS (CI) m/z 402 ($\text{M}^+ + 1$). HR-MS (CI) calcd. for $\text{C}_{22}\text{H}_{28}\text{NO}_4\text{S}$ ($\text{M}^+ + 1$) 402.1739, found 402.1744.

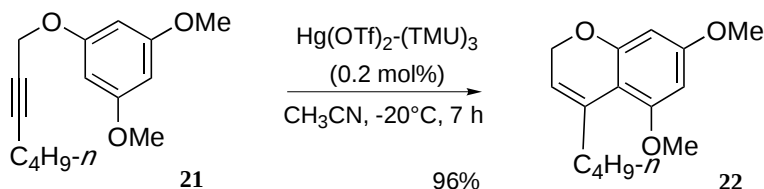


18 : IR (neat) 2956, 2861, 2835, 1603, 1493, 1456, 1153, 1054 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.89 (3 H, t, $J = 7.4$ Hz), 1.33-1.50 (4 H, m), 2.14 (2 H, dt, $J = 2.5, 6.9$ Hz), 2.43 (2 H, dt, $J = 2.5, 7.7$ Hz), 2.78 (2 H, t, $J = 7.7$ Hz), 3.79 (3 H, s), 6.73-6.82 (3 H, m), 7.20 (1 H, dt, $J = 0.8, 7.7$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 13.52, 18.33, 20.84, 21.82, 31.08, 35.60, 54.84, 79.26, 80.81, 111.30, 114.08, 120.68, 129.08, 142.48, 159.46. MS (CI) m/z 217 ($\text{M}^+ + 1$).

HR-MS (CI) calcd. for $C_{15}H_{21}O$ ($M^+ + 1$) 217.1593, found 217.1593.

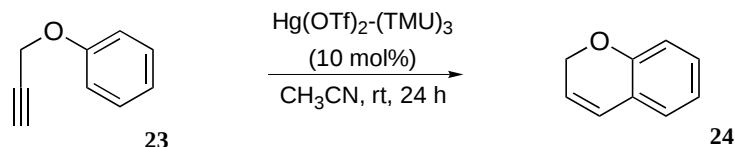
19 : IR (neat) 2930, 2860, 2832, 1607, 1498, 1143, 1042 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 0.92 (3 H, t, $J = 7.1$ Hz), 1.31-1.43 (2 H, m), 1.45-1.55 (2 H, m), 2.19-2.26 (2 H, m), 2.41 (2 H, dt, $J = 1.1, 7.7$ Hz), 2.71 (2 H, t, $J = 7.7$ Hz), 3.81 (3 H, s), 5.72 (1 H, tt, $J = 1.1, 4.4$ Hz), 6.71 (1 H, br s), 6.73 (1 H, dd, $J = 2.2, 7.1$ Hz), 7.18 (1 H, dd, $J = 2.2, 9.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.99, 22.64, 23.07, 29.00, 30.65, 32.54, 55.03, 110.67, 113.69, 121.97, 123.70, 128.12, 136.14, 138.52, 158.13. MS (CI) m/z 217 ($M^+ + 1$). HR-MS (CI) calcd. for $C_{15}H_{21}O$ ($M^+ + 1$) 217.1592, found 217.1583.

20 : IR (neat) 2932, 2856, 2833, 1569, 1468, 1088, 778 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 0.90 (3 H, t, $J = 7.2$ Hz), 1.28-1.42 (4 H, m), 2.05-2.12 (2 H, m), 2.61-2.69 (4 H, m), 3.80 (3 H, s), 5.89 (1 H, t, $J = 5.1$ Hz), 6.80 (1 H, t, $J = 7.8$ Hz), 7.11 (2 H, t, $J = 7.8$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.10, 22.64, 22.80, 30.15, 31.67, 36.29, 55.30, 110.09, 120.38, 124.08, 126.00, 127.02, 137.73, 140.43, 156.16. MS (CI) m/z 217 ($M^+ + 1$). HR-MS (CI) calcd. for $C_{15}H_{21}O$ ($M^+ + 1$) 217.1592, found 217.1595.



21 : IR (neat) 2957, 2871, 2840, 2226, 1606, 1476, 1161, 1066 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 0.89 (3 H, t, $J = 7.1$ Hz), 1.33-1.54 (4 H, m), 2.23 (2 H, dt, $J = 2.2, 7.0$ Hz), 3.76 (6 H, s), 4.62 (2 H, t, $J = 2.2$ Hz), 6.11 (1 H, t, $J = 2.2$ Hz), 6.15 (2 H, d, $J = 2.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.45, 18.37, 21.80, 30.40, 55.12, 55.12, 56.40, 74.62, 88.13, 93.28, 93.54, 93.54, 159.59, 161.25, 161.25. MS (CI) m/z 249 ($M^+ + 1$). HR-MS (CI) calcd. for $C_{15}H_{21}O_3$ ($M^+ + 1$) 249.1490, found 249.1495.

22 : IR (neat) 2956, 2856, 1201, 1157, 1128, 819 cm^{-1} . 1H NMR (600 MHz, $CDCl_3$) δ 0.88 (3 H, t, $J = 7.1$ Hz), 1.28-1.38 (4 H, m), 2.56 (2 H, dt, $J = 1.1, 7.1$ Hz), 3.77 (3 H, s), 3.78 (3 H, s), 4.46 (2 H, dt, $J = 1.1, 4.4$ Hz), 5.46 (1 H, tt, $J = 1.1, 4.4$ Hz), 6.09 (1 H, d, $J = 2.5$ Hz), 6.13 (1 H, d, $J = 2.5$ Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.00, 22.54, 31.20, 34.53, 55.26, 55.27, 64.88, 92.80, 93.88, 107.19, 114.86, 136.19, 157.66, 157.83, 160.41. MS (EI) m/z 248 (M^+). HR-MS (EI) calcd. for $C_{15}H_{20}O_3$ (M^+) 248.1412, found 248.1418.



23 : IR (neat) 3296, 2121, 2055, 1991, 1933, 1843, 1772, 1698, 1601, 1497, 1456, 1080, 1040 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 2.52 (1 H, t, $J = 2.5$ Hz), 4.70 (2 H, d, $J = 2.5$ Hz), 6.97-7.02 (3 H, m), 7.25-7.34 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.59, 75.44, 78.57, 114.78, 114.78, 121.46, 129.39, 129.39, 157.42. MS (CI) m/z 133 ($M^+ + 1$). HR-MS (CI) calcd. for C_9H_9O ($M^+ + 1$) 133.0653, found 133.0650.

24 : IR (neat) 3043, 2832, 1605, 1487 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 4.80 (2 H, dd, $J = 1.9, 3.6$ Hz), 5.74 (1 H, dt, $J = 3.6, 9.9$ Hz), 6.39 (1 H, dt, $J = 0.4, 9.9$ Hz), 6.76 (1 H, br d, $J = 8.0$ Hz), 6.84 (1 H, dt, $J = 1.1, 7.4$ Hz), 6.93 (1 H, dd, $J = 1.8, 7.4$ Hz), 7.08 (1 H, dt, $J = 1.8, 8.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.47, 115.69, 121.28, 121.94, 122.36, 124.54, 126.54, 129.09, 154.05. MS (CI) m/z 133 ($M^+ + 1$). HR-MS (CI) calcd. for C_9H_9O ($M^+ + 1$) 133.0653, found 133.0636.