Supporting Information

A Palladium-catalyzed Cyclization-Oxidation Sequence: Synthesis of Bicyclo[3.1.0]Hexanes and Evidence for S_N2 C-O Bond Formation

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General: NMR spectra were recorded on a Bruker ARX 300 spectrometer, operating at 300 MHz for ¹H NMR, 75 MHz for ¹³C NMR were reported downfield from CDCl₃ (δ: 7.27 ppm) for ¹H NMR. For ¹³C NMR, chemical shifts were reported in the scale relative to the solvent of CDCl₃ (δ: 77.0 ppm) used as an internal reference. Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector. Column chromatographies were performed with silica gel Fluka 60 (70-230 mesh ASTM).

General Procedure for Pd(OAc)₂ Catalyzed Cyclization-Oxidation of 1,6-Enyne 1: substrate **1** (0.3 mmol), Pd(OAc)₂ (6.8 mg, 10 mmol%) and PhI(OAc)₂ (193 mg, 2 equiv.) were added to HOAc (3 mL) in Schlenk tube. The mixture was stirred at 80 °C and monitored by TLC. When the starting material was disappeared the reaction was cooled and quenched with H₂O (30 mL), extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was dried over Na₂SO₄. Filtration, evaporation, and purification by silica gel column chromatography (AcOEt:Hexane = 1:10 to 1:2) gave the product **2**.

¹H NMR (CDCl₃, 300 MHz) δ: 1.44 (t, *J* = 5.1 Hz, 1H), 2.12 (dd, *J* = 4.8, 7.8 Hz, 1H), 2.79-2.86 (m, 1H), 4.34 (d, *J* = 9.6 Hz, 1H), 4.57 (dd, *J* = 4.8, 9.6 Hz, 1H), 7.45-7.51 (m, 2H), 7.57-7.63 (m, 1H), 7.87-7.90 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ: 19.09, 27.07, 35.72, 67.89, 128.44, 129.09, 133.62, 135.47, 172.72, 192.01; MS (*m/z*): 202 (*M*⁺); HRMS Calcd for C₁₂H₁₀O₃ 202.0630, Found 202.0621.

¹H NMR (CDCl₃, 300 MHz) δ: 1.41 (dd, *J* = 4.2, 5.7 Hz, 1H), 2.06 (dd, *J* = 4.2, 8.1 Hz, 1H), 2.58 (s, 3H), 2.76-2.83 (m, 1H), 4.18 (d, *J* = 9.3 Hz, 1H), 4.34 (dd, *J* = 4.8, 9.6 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ:

24.21, 29.31, 29.87, 36.54, 67.18, 172.79, 200.58; MS (m/z): 140 (M^+); HRMS Calcd for $C_7H_8O_3$ 140.0473 Found 140.0473.

1H NMR ($CDCl_3$, 300 MHz) δ : 0.91 (t, J = 7.2 Hz, 3H), 1.27-1.41 (m, 3H), 1.52-1.64 (m, 2H), 2.04 (dd, J = 4.2, 8.1 Hz, 1H), 2.72-2.78 (m, 1H), 2.80-2.89 (m, 1H), 3.06-3.17 (m, 1H), 4.18 (d, J = 9.3 Hz, 1H), 4.33 (dd, J = 4.8, 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ : 13.81, 22.11, 23.73, 25.44, 29.58, 36.12, 41.27, 67.18, 172.78, 202.80; MS (m/z): 182 (M^+); HRMS Calcd for $C_{10}H_{14}O_3$ 182.0943, Found 182.0937.

1H NMR ($CDCl_3$, 300 MHz) δ : 1.33 (t, J = 4.8 Hz, 1H), 2.47 (dd, J = 3.0, 6.0 Hz, 1H), 2.65-2.72 (m, 1H), 3.86 (s, 3H), 4.29 (d, J = 9.6 Hz, 1H), 4.44 (dd, J = 4.2, 9.0 Hz, 1H), 6.95 (d, J = 9.0 Hz, 1H), 7.03-7.09 (m, 1H), 7.48-7.55 (m, 1H), 7.64 (dd, J = 2.1, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ : 18.46, 31.04, 38.19, 55.21, 68.97, 111.24, 121.29, 126.52, 130.67, 134.31, 158.06, 173.59, 192.86; MS (m/z): 232 (M^+); HRMS Calcd for $C_{13}H_{12}O_4$ 232.0736, Found 232.0733.

1H NMR ($CDCl_3$, 300 MHz) δ : 0.86 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 5.1 Hz, 1H), 1.20-1.1.33 (m, 2H), 1.41-1.54 (m, 2H), 1.91 (dd, J = 4.2, 7.8 Hz, 1H), 2.45-2.52 (m, 4H), 2.71-2.82 (m, 1H), 2.94-3.05 (m, 1H), 3.90 (d, J = 3.0 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ : 13.88, 21.75, 22.17, 23.76, 24.11, 25.53, 38.83, 41.59, 46.86, 128.09, 129.84, 134.74, 145.53, 169.44, 203.14; MS (m/z): 335 (M^+); HRMS Calcd for $C_{17}H_{21}NO_4S$ 335.1191, Found 335.1181.

1H NMR ($CDCl_3$, 300 MHz) δ : 1.37 (t, J = 5.1 Hz, 1H), 1.98 (dd, J = 4.8, 7.8 Hz, 1H), 2.46 (s, 3H), 2.52-2.56 (m, 1H), 4.01-4.11 (m, 2H), 7.31-7.37 (m, 4H), 7.51-7.57 (m, 1H), 7.69-7.72 (m, 2H), 7.91 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ : 19.20, 21.37, 21.65, 38.55, 47.25, 128.08, 128.30, 129.19, 129.74, 133.56, 134.35, 135.37, 145.43, 169.25, 192.17; MS (m/z): 355 (M^+); HRMS Calcd for $C_{19}H_{17}NO_4S$ 355.0878, Found 355.0849.

^1H NMR (CDCl_3 , 300 MHz) δ : 1.24 (dd, $J = 4.2, 5.1$ Hz, 1H), 1.57 (dd, $J = 3.9, 8.1$ Hz, 1H), 2.39-2.45 (m, 1H), 3.84-3.97 (m, 1H), 3.98 (d, $J = 8.4$ Hz, 1H), 4.22 (d, $J = 8.4$ Hz, 1H), 7.43-7.50 (m, 2H), 7.52-7.58 (m, 1H), 7.72-7.76 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 18.88, 29.37, 38.79, 68.72, 70.26, 127.76, 128.47, 132.37, 138.22, 200.39; MS (m/z): 188 (M^+); HRMS Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$ 188.0837, Found 188.0819.

^1H NMR (CDCl_3 , 300 MHz) δ : 1.31 (t, $J = 5.1$ Hz, 1H), 1.45 (dd, $J = 4.8, 8.1$ Hz, 1H), 2.25-2.31 (m, 1H), 2.42 (s, 3H), 3.17 (dd, $J = 3.9, 9.3$ Hz, 1H), 3.29 (d, $J = 10.2$ Hz, 1H), 3.63 (d, $J = 9.6$ Hz, 1H), 3.98 (d, $J = 9.3$ Hz, 1H), 7.29-7.32 (m, 2H), 7.40-7.46 (m, 2H), 7.52-7.58 (m, 1H), 7.63-7.68 (m, 4H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 19.45, 21.44, 26.06, 36.87, 48.80, 50.68, 127.44, 127.81, 128.54, 129.72, 132.60, 132.81, 137.37, 143.78, 199.37; MS (m/z): 188 (M^+); HRMS Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3\text{S}$ 341.1086, Found 341.0156.

^1H NMR spectrum of compound 6 is show as following:

Tong/ txf- 1- 123
 Au1H CDC13 /opt/topspin 0701/34

The ratio of two isomers is determined to 1.6:1 based on the integration. $J_{\text{HaHb}} = 4.2$ Hz for one of isomers. For the other, $J_{\text{HaHb}} = 4.8$ Hz. According to the literature,¹ the stereochemistry of Ha and Hb is assigned to be syn.

¹ (a) Liu, J.; Murray, E. M.; Young, V. G. *Chem. Commun.* **2003**, 15, 1904 - 1905. (b) Juaristi, E.; Beck, A. K.; Hansen, J.; Matt, T.; Mukhopadhyay, T. *Synthesis* **1993**, 12, 1271-1290. (c) Mukai, C.; Cho, W. J.; Kim, I.; Kido, M.; Hanaoka, M. *Tetrahedron* **1991**, 47, 3007-3036.

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Tong/ txf- 1- 98a

Au13C CDCl3 /opt/topspin 0611 1