Supporting Information

Rhodium Catalyzed Cyclization-cycloaddition Reactions of Enynebezaldehydes: Construction of Polycyclic Ring System

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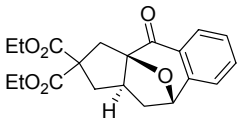
A General Procedure:

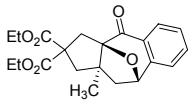
All solvents were reagent grade. All chemicals were purchased from Aldrich Chemical Co. Reactions were normall y carried out under argon atmosphere in flame-dried glassware. Merck silica gel 60 (partial size 0.04-0.063 mm) w as employed for flash chromatography. The sample was analyzed and/or separated on a μ-Porasil column (25 cm x 1.0 cm) by elution with gradient of ethyl acetate and hexane. The flow rate of the indicated elution solvent is maint ained at 5 mL/min, and the retention time of a compound is recorded. ^{1}H NMR and COSY spectra were obtained i n $CDCl_3$ unless otherwise noted at 400 MHz. ^{13}C NMR spectra, HMBC, HMQC and DEPT experiments were obta ined at 100 MHz.

General Experimental Procedure for the preparation of compound 11a-i:

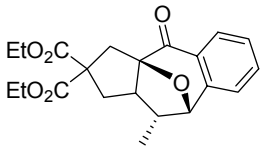
Into a 10 mL round bottomed flask, 1 mmol of enynebenzaldehyde, 5 mole% $[Rh(COD)Cl]_2$, dimmer and 10 mole % DPPP, was taken. To this 5 % aqueous toluene (2 mL) was added through the glass syringe. Reaction mixture fir st, stirred for 10 min at room temperature and then kept in preheated oil bath at 100-110 ˚C. After completion of th e reaction, it was cooled, diluted with diethylether and filtered through celite. The solvent was evaporated and subj ected for column chromatography to get pure compound.



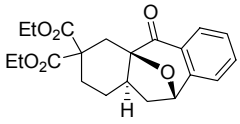
Spectroscopic data of compound 2a: (Colorless syrupy liquid, *Rf* = 0.55, 25 % EtOAc-hexane). **IR (neat):** 2980, 1728, 1699, 1602, 1445, 1366, 1268, 1247, 1182, 1093, 862 cm^{-1}**; ^{1}H NMR ($CDCl_3$):** δ 8.00 (d, J =7.6 Hz, 1 H), 7.50 (t, J =8.1 Hz, 1 H), 7.36 (t, J =7.20 Hz , 1 H), 7.17 (d, J = 7.2 Hz, 1 H), 5.31 (d, J = 6.4 Hz, 1 H), 4.17 (m, 4 H), 3. 28 (d, J = 14.8 Hz, 1 H), 2.66-2.78 (m, 2 H), 2.44 (dd, J = 14.4, 4.4 Hz, 1 H), 2.39 (m, 2 H), 2.15 (dt, J = 9.2, 6.4, 2.8 Hz, 1 H), 1.21 (t, J = 7.2 Hz) **^{13}C NMR ($CDCl_3$):** δ 193.77, 171.07, 171.03, 146.97, 133.98, 128.49, 128.06, 127.30, 124.04, 97.22, 80.18, 62.42, 62.10, 61.91, 44.18, 39.95, 37.81, 14.49, 14.44 ; **MS (m/z) HRMS: exact mass calculated for**: $C_{20}H_{22}O_6$ (M^+): 358.1416; **found.** 358.1421.



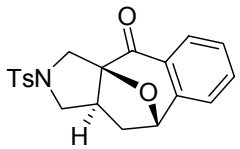
Spectroscopic data of compound 2b: (Colorless syrupy liquid, *Rf* = 0.55, 25 % EtOAc-hexane). **IR (neat):** 2979, 1727, 1697, 1599, 1451, 1345, 1162, 1093, 1011, 911 cm^{-1}**; ^{1}H NMR ($CDCl_3$):** δ 8.01 (d, J = 7.6 Hz, 1 H), 7.51 (t, J = 7.6 Hz ,1 H), 7.15 (d, J = 7.60 Hz, 1 H), 5.19 (d, J = 6.80 Hz, 1 H), 4.16-4.25 (m, 4 H), 3.19 (d, J = 14.80 Hz, 1 H), 3.02(d, J = 13.6 Hz, 1 H), 2.81 (dd, J = 7.6, 6.8 Hz, 1 H), 2.71 (d, J = 14.6 Hz, 1 H), 1.91 (d, J = 14.6 Hz, 1 H), 1.81 (d, J = 12.0 Hz, 1 H), 1.26 (t, J = 7.2 Hz, 3 H), 0.92 (s, 3 H). **^{13}C NMR ($CDCl_3$):** δ 193.97, 171.28, 171.09, 146.74, 133.89, 129.08, 127.94, 126.66, 123.91,98.59, 79.02, 61.77,61.50, 59.56, 50.08, 49.03, 47.18, 36.96, 29.67, 26.34, 14.00, 13.98 ; **MS (m/z): HRMS: exact mass calculated for**: $C_{21}H_{24}O_6$ (M^+): 372.1573; **found.** 372.1561.



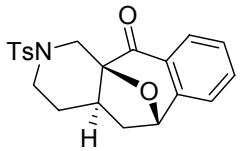
Spectroscopic data of compound 2c: (Colorless syrupy liquid, *Rf* = 0.51, 25 % EtOAc-hexane). **IR (neat):** 2978, 1729, 1700, 1603, 1459, 1366, 1247, 1183, 1110, 1016, 913 cm^{-1}**; ^{1}H NMR ($CDCl_3$):** δ 8.05 (d, J = 7.6 Hz, 1 H), 7.52 (t, J = 7.2 Hz, 1 H), 7.42 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1 H), 5.07 (d, J = 6.4 Hz, 1 H), 4.17-4.27 (m, 4 H), 3.20 (d, J = 12.8 Hz, 1 H), 2.63-2.78 (m, 1 H), 2.59-2.60 (t, J = 2.4 Hz, 2 H), 2.33 (dd, J = 10.0, 4.8 Hz, 1 H), 2.13-2.15 (m, 1 H), 1.27 (t, J = 7.2 Hz, 6 H), 0.76 (d, J = 6.8 Hz, 3 H). **^{13}C NMR ($CDCl_3$):** δ 193.94, 171.06, 143.45, 133.28, 129.19, 128.22, 127.37, 125.98, 97.34, 83.85, 62.35, 62.11, 61.91, 52.37, 45.15, 38.50, 37.85, 16.29, 12.48, 14.43. **MS (m/z) HRMS: exact mass calculated for**: $C_{21}H_{24}O_6$ (M^+): 372.1573; **found.** 372.1563.



Spectroscopic data of compound 2d: (Colorless syrupy liquid, *Rf* = 0.55, 25 % EtOAc-hexane). **IR (neat):** 2980, 2850, 1730, 1689, 1610, 1462, 1379, 1246, 1247, 1174 1108, 908 cm^{-1}**; ^{1}H NMR ($CDCl_3$):** δ 8.09 (d, J =8.6 Hz, 1 H), 7.50 (t, J = 8.1 Hz, 1 H), 7.23 (t, J = 8.5 , 1 H), 7.15 (d, J = 8.2 Hz, 1 H), 5.31 (d, J = 7.2 Hz, 1 H), 4.19-4.22 (m, 4 H), 3.33 (d, J = 14.3 Hz, 1H), 2.96-2.98 (m, 2 H), 2.34 (dd, J = 4.4, 4.4 Hz, 1H),2.23, (m, 2 H), 2.23 (m, 2 H), 2.14 (dt, J = 10.2, 7.2, 2.8 Hz, 1 H), 1.21 (t, J = 7.2 Hz, 6 H) **^{13}C NMR ($CDCl_3$):** δ 193.87, 176.37, 170.10, 140.69, 134.7, 132.75, 128.49, 128.26, 97.22, 80.18, 61.01 59.42, 59.10, 44.18, 38.29, 37.81, 26.23, 23.8, 14.50, 14.24 ; **MS (m/z) HRMS: exact mass calculated for**: $C_{21}H_{24}O_6$ (M^+): 372.1573; **found.** 372.1481**.**



Spectroscopic data of compound 2e: (Colorless syrupy liquid, *Rf* = 0.55, 50 % EtOAc-hexane). **IR (neat):** 2946, 2866, 1697, 1597, 1344, 1162, 1093, 1003, 912, 783 cm^{-1}**; ^{1}H NMR ($CDCl_3$):** δ 7.97 (d, J = 7.6 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 2 H), 7.51 (t, J = 6.4 Hz, 1 H), 7.39-7.41 (m 3 H), 7.18 (d, J = 6.8 Hz, 1 H), 5.39 (d, J = 6.4 Hz, 1 H), 3.99 (d, J = 11.20 Hz, 1 H), 3.45-3.55 (m, 2 H), 3.23-3.26 (m, 1 H), 2.59-2.64 (m, 1 H), 2.44 (s, 3 H), 2.12-2.23 (m, 2 H). **^{13}C NMR ($CDCl_3$):** δ 191.42, 146.08, 143.74, 134.12, 129.64, 128.12, 127.97, 127.88, 127.21, 123.86, 95.30, 80.36, 53.92, 51.39, 44.11, 38.14, 21.71; **MS (m/z) HRMS: exact mass calculated for**: $C_{20}H_{19}NO_4S$ (M+):369.1035; **found.** 369.1029.



Spectroscopic data of compound 2f: (Colorless syrupy liquid, *Rf* = 0.55, 50 % EtOAc-hexane). **IR (neat):** 2925, 1691, 1642, 1598, 1460, 1344, 1284, 1159, 1091, 793 cm-1**; 1H NMR ($CDCl_3$):** δ 7.94 (d, J = 8.2 Hz, 1 H), 7.69 (d, J = 8.0 Hz, 2 H), 7.52 (t, J = 7.6 Hz, 1 H), 7.31 (t, J = 7.2 Hz, 1 H), 7.31 (d, J= 8.0 Hz, 2 H), 7.19 (d, J = 8.00 Hz, 2 H), 5.25 (d, J = 6.80 Hz, 1 H), 4.10 (q, J = 7.20, 6.80 Hz 1 H), 3.96 (d, J = 13.2 Hz, 1 H), 3.66-3.68 (m, 1 H), 3.56 (d, J = 12.9 Hz, 1H), 2.65-2.68 (m, 1 H), 2.44 (s, 3 H), 1.98-2.07 (m, 5 H), 2.00 (m, 1 H). **13C NMR ($CDCl_3$):** δ 194.97, 148.13, 143.25, 134.08, 133.85, 129.64, 129.47, 127.82, 127.82, 127.53, 127.47, 122.99, 85.56, 75.98, 45.05, 43.03, 40.08, 34.42, 29.15, 21.66, 14.32 ; **MS (m/z) HRMS: exact mass calculated for**: $C_{21}H_{21}NO_4S$ (M+):383.1153 ; **found.** 383.1220.