Supporting Information

Phosphine Mediated Reductive Condensation of γ -Acyloxy Butynoates: A Diversity Oriented Strategy for the Construction of Substituted Furans

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I. Experimental Procedure

General: Ethyl acetate was degassed with Ar prior to use. All reactions were performed under Ar atmosphere unless otherwise noted. Chemical reagents were purchased from Aldrich chemical companies and used without further purification, unless otherwise noted. Deuterated solvents were used as received from Cambridge Isotope Laboratories. Analytical TLC was performed on EM Reagents 0.25mm silica gel 60-F plates, and visualized under UV light. Flash chromatography was performed on silica gel 60 (200-400 mesh). NMR spectra were recorded on a Varian UNITY+ spectrometer. ^1H NMR spectra were obtained at either 400 MHz or 300 MHz, as indicated. ^{13}C NMR spectra were obtained at either 100MHz or 75 MHz, as indicated. High resolution mass spectra were obtained on a Micromass ZAB-E spectrometer. FT-IR spectra were obtained using a Nicolet Impact 410 spectrometer. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected.

General Procedure for Synthesis of Substituted Furans: A solution of the propargyl ester (100 mol%) in ethyl acetate (0.1 M) was degassed with Ar for 3 min. Triphenylphosphine (120 mol%) was added to the solution of substrate. The reaction vessel was sealed, heated to 110 °C, and allowed to stir until complete consumption of starting material was observed. The reaction mixture was evaporated onto silica gel and subjected to purification by flash chromatography (SiO_2 : Et_2O -Hexane) to afford the desired furan.

Amended Procedures: For substrate **3a**, the reaction was conducted at ambient temperature. For substrate **6a**, the reaction was conducted at ambient temperature using (*m*-Tol) $_3\text{P}$ (120 mol%) in benzene (0.1 M). For substrate **11a**, the reaction was conducted at ambient temperature using (*m*-Tol) $_3\text{P}$ (120 mol%) in ethyl acetate (0.1 M). For substrate **16a**, the reaction was conducted at ambient temperature using triphenylphosphine (120 mol%) in benzene (0.1 M).

II. Spectroscopic Data for Propargylic Ester Substrates

^1H NMR (400 MHz, CDCl_3): δ 1.28 (t, $J = 7.2$ Hz, 3H), 4.22 (q, $J = 7.2$ Hz, 2H), 5.01 (s, 2H), 7.43 (m, 2H), 7.57 (dt, $J = 1.37, 7.5$ Hz, 1H), 8.04 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 13.9, 51.7, 62.3, 78.1, 80.8, 128.5, 128.9, 129.8, 133.5, 152.8, 165.5.

HRMS: Calcd $[\text{M}+1]$ for $\text{C}_{13}\text{H}_{12}\text{O}_4$: 233.0814; Found: 233.0804.

FTIR (film): 3406, 2325, 2249, 1701, 1639, 1454, 1368, 1255, 1096, 1020, 707 cm^{-1} .

(^1H and ^{13}C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.30 (t, *J* = 7.2 Hz, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 5.07 (s, 2H), 8.22 (dt, *J* = 2.1, 9.0 Hz, 2H), 8.29 (dt, *J* = 2.1, 9.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 14.0, 52.6, 62.5, 78.7, 79.8, 123.7, 131.1, 134.2, 150.9, 152.7, 163.7.

HRMS: Calcd [M+1] for C₁₃H₁₁NO₆: 278.0665; Found: 278.0662.

FTIR (film): 3430, 3096, 2358, 2243, 1725, 1716, 1620, 1340, 1245, 1152, 1066, 723 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

^1H NMR (400 MHz, CDCl_3): δ 2.34(s, 3H), 5.09 (s, 2H), 8.20 (dt, $J = 2.1, 8.9$ Hz, 2H), 8.27 (dt, $J = 2.1, 9.0$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 32.4, 52.6, 83.8, 85.8, 123.6, 131.0, 134.2, 150.8, 163.7, 183.4.

HRMS: Calcd $[\text{M}+1]$ for $\text{C}_{12}\text{H}_{19}\text{NO}_5$: 248.0559; Found: 248.0568.

FTIR (film): 3416, 2342, 1736, 1665, 1521, 1342, 1255, 1106, 1020, 963, 871, 718 cm^{-1}

MP: 102-103 $^\circ\text{C}$

(^1H and ^{13}C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.27 (t, *J* = 7.2 Hz, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 5.14 (s, 2H), 9.14 (d, *J* = 2.1 Hz, 2H), 9.21 (t, *J* = 2.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 13.8, 53.3, 62.4, 79.0, 79.0, 122.9, 129.6, 132.5, 148.6, 152.4, 161.6.

HRMS: Calcd [M+1] for C₁₃H₁₀N₂O₈: 323.0515; Found: 323.0499.

FTIR (film): 3432, 3098, 2356, 2244, 1752, 1623, 1537, 1342, 1245, 1153, 1065, 723 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

^1H NMR (400 MHz, CDCl_3): δ 1.29 (t, $J = 7.2$ Hz, 3H), 4.23 (q, $J = 7.2$ Hz, 2H), 5.01 (s, 2H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.90 (d, $J = 8.5$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 13.9, 52.0, 62.4, 78.3, 80.5, 127.8, 128.8, 131.4, 131.9, 152.8, 164.8.

HRMS: Calcd $[M+1]$ for $\text{C}_{13}\text{H}_{11}\text{BrO}_4$: 310.9919; Found: 310.9928.

FTIR (film): 3411, 2310, 2232, 1700, 1630, 1458, 1370, 1255, 1096, 1020, 721 cm^{-1} .

(^1H and ^{13}C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.28(m, 3H), 4.22 (m, 2H), 5.05 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 13.9, 53.1, 62.4, 78.9, 106.8 (m), 136.5 (m), 139.4 (m), 142.3 (m), 144.5 (m), 147.0 (m), 152.6, 158.2.

HRMS: Calcd [M+1] for C₁₃H₇O₄F₅: 323.0343; Found: 323.0338.

FTIR (film): 3421, 2996, 2243, 1746, 1665, 1506, 1419, 1362, 1326, 1260, 1205, 1081, 1004, 953, 748 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.32 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 5.08 (s, 2H), 7.43 (m, 1H), 8.33 (dt, *J* = 2.0, 8.0 Hz, 1H), 8.82 (dd, *J* = 1.7, 4.8 Hz, 1H), 9.26 (t, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.0, 52.1, 62.4, 78.5, 80.1, 123.4, 125.0, 137.3, 151.1, 152.7, 154.0, 164.3.

HRMS: Calcd [M+1] for C₁₂H₁₁NO₄: 234.0766; Found: 234.0777.

FTIR (film): 3155, 2985, 2253, 1734, 1728, 1264, 1109, 908, 732, 651 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.28 (t, *J* = 7.2, Hz 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.99 (s, 2H), 6.51 (dd, *J* = 1.7, 3.4 Hz, 1H), 7.23 (dd, *J* = 0.7, 3.4 Hz, 1H), 7.59 (dd, *J* = 0.7, 1.7 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 13.9, 51.5, 62.3, 78.3, 80.3, 112.1, 119.3, 143.4, 147.1, 152.4.

HRMS: Calcd [M+1] for C₁₁H₁₀O₅: 223.0606; Found: 223.0608.

FTIR (film): 3421, 2981, 2244, 1716, 1639, 1470, 1360, 1255, 1188, 1091, 1055, 763 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.29 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.96 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 13.9, 13.9, 53.3, 62.4, 63.7, 78.6, 79.1, 152.5, 156.6, 156.7.

HRMS: Calcd [M+1] for C₁₀H₁₂O₆: 229.0712; Found: 229.0701.

FTIR (film): 3411, 2980, 2929, 2351, 2249, 1783, 1751, 1716, 1383, 1326, 1265, 1153, 1020, 943, 873, 758 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

^1H NMR (400 MHz, CDCl_3): δ 1.28 (t, $J = 7.2$ Hz, 3H), 1.88 (dd, $J = 1.7, 6.8$ Hz, 3H), 4.21 (q, $J = 7.2$ Hz, 2H), 4.81 (s, 2H), 5.83 (dq, $J = 1.7, 15.6$ Hz, 1H), 7.03 (dq, $J = 7.0, 15.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 13.9, 18.1, 51.0, 62.2, 77.8, 81.0, 121.7, 146.8, 152.8, 165.2.

HRMS: Calcd $[\text{M}+1]$ for $\text{C}_{10}\text{H}_{12}\text{O}_4$: 197.0814; Found: 197.0812.

FTIR (film): 2970, 2233, 1705, 1654, 1334, 1368, 1260, 1158, 1020, 953, 748 cm^{-1} .

(^1H and ^{13}C NMR Spectra on following page)

^1H NMR (400 MHz, CDCl_3): δ 1.32 (t, $J = 7.2$ Hz, 3H), 1.33 (t, $J = 7.2$ Hz, 3H), 4.26 (q, $J = 7.2$ Hz, 2H), 4.38 (q, $J = 7.2$ Hz, 2H), 4.92 (s, 2H), 6.86 (d, $J = 15.7$ Hz, 1H), 6.93 (d, $J = 15.7$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 12.9, 14.0, 52.0, 61.5, 62.3, 78.4, 78.4, 79.8, 131.8, 135.2, 152.6, 163.8, 164.5.

HRMS: Calcd $[\text{M}+1]$ for $\text{C}_{12}\text{H}_{14}\text{O}_6$: 255.0869; Found: 255.0860.

FTIR (film): 3265, 3055, 2986, 2305, 2254, 1721, 1423, 1369, 1265, 1152, 1029, 980, 909, 739, 651 cm^{-1} .

(^1H and ^{13}C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.07 (dd, *J* = 5.6, 6.8 Hz, 6H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.19 (m, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 5.42 (dd, *J* = 1.0, 5.6 Hz, 1H), 8.09 (d, *J* = 1.0 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃): δ 13.9, 17.5, 17.9, 32.1, 62.2, 67.4, 77.8, 82.0, 152.8, 159.5.

HRMS: Calcd [M+1] for C₁₀H₁₄O₄: 199.0970; Found: 199.0979.

FTIR (film): 3441, 3324, 3058, 2991, 1711, 1434, 1271, 1163, 897, 738 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.32(t, *J* = 7.2 Hz, 3H), 1.78 (ddd, *J* = 0.7, 1.7, 6.8 Hz, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 5.58 (ddq, *J* = 1.7, 6.8, 15.1 Hz, 1H), 6.06 (m, 2H), 8.05 (d, *J* = 1.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 13.9, 17.5, 62.3, 62.9, 78.0, 81.5, 123.7, 133.9, 152.8, 159.2.

HRMS: Calcd [M+1] for C₁₀H₁₂O₄: 197.0814; Found: 197.0817.

FTIR (film): 3503, 3401, 3234, 2985, 2942, 2253, 1705, 1446, 1368, 1252, 1149, 964, 907, 730, 649 cm⁻¹

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.16(d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.31 (m, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 5.63 (d, *J* = 5.8 Hz, 1H), 9.17 (d, *J* = 2.1 Hz, 2H), 9.27 (t, *J* = 1.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 13.9, 17.7, 18.1, 32.4, 62.3, 70.6, 78.5, 81.2, 122.8, 129.5, 133.0, 148.6, 152.6, 161.4.

HRMS: Calcd [M+1] for C₁₆H₁₆N₂O₈: 365.0985; Found: 365.0982.

FTIR (film): 3300, 3099, 2973, 2938, 2244, 1715, 1630, 1549, 1463, 1346, 1249, 1162, 1078, 980, 922, 734 cm⁻¹

MP: 82-83 °C

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.33(t, *J* = 7.2 Hz, 3H), 1.84 (m, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 5.74 (m, 1H), 6.20 (m, 1H), 6.23 (m, 1H), 9.18 (d, *J* = 2.1 Hz, 2H), 9.26 (t, *J* = 2.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 13.9, 17.7, 62.5, 66.1, 78.9, 80.8, 122.8, 123.3, 130.0, 133.1, 135.4, 148.7, 152.7, 161.2.

HRMS: Calcd [M+1] for C₁₆H₁₄N₂O₈: 363.0828; Found: 363.0834.

FTIR (film): 3258, 3055, 2984, 2306, 1714, 1548, 1422, 1346, 1265, 1158, 896, 739 cm⁻¹

MP: 96-97 °C

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.33(t, *J* = 7.0 Hz, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 7.01 (s, 1H), 7.04 (dd, *J* = 3.8, 5.1 Hz, 1H), 7.32 (m, 1H), 7.44 (dd, *J* = 1.0, 5.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 13.9, 62.2, 78.6, 80.1, 106.8 (m), 127.0, 128.5, 129.2, 135.9, 136.4 (m), 139.0 (m), 142.4 (m), 144.5 (m), 147.1 (m), 152.6, 157.6.

HRMS: Calcd [*M*⁺] for C₁₇H₉F₅O₄S: 404.0142; Found (FAB): 404.0144.

FTIR (film): 3945, 3693, 3055, 2986, 2685, 2306, 2249, 1743, 1716, 1651, 1524, 1502, 1423, 1369, 1338, 1265, 1212, 1099, 1005, 947, 898, 857, 840, 740, 707 cm⁻¹

(¹H and ¹³C NMR Spectra on following page)

III. Spectroscopic Data for Substituted Furans

¹H NMR (400 MHz, CDCl₃): δ 1.32 (t, *J* = 7.1 Hz, 3H), 4.29 (q, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 1.7 Hz, 1H), 7.41 (m, 4H), 7.97 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 14.2, 60.4, 112.9, 113.8, 128.0, 128.3, 129.3, 129.7, 141.1, 157.4, 163.5.

HRMS: Calcd [M+1] for C₁₃H₁₂O₃: 217.0865; Found: 217.0861.

FTIR (film): 3416, 2970, 2346, 1721, 1629, 1486, 1168, 1127, 1071, 769, 691 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.35 (t, *J* = 7.2 Hz, 3H), 4.32 (q, *J* = 7.1 Hz, 2H), 6.89 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 8.24 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): δ 14.2, 61.0, 113.8, 116.7, 123.4, 128.8, 135.4, 142.6, 147.6, 154.3, 163.1.

HRMS: Calcd [M+1] for C₁₃H₁₁O₅: 262.0715; Found: 262.0714.

FTIR (film): 3431, 2991, 2356, 1649, 1521, 1281, 1153, 1066, 861, 764 cm⁻¹.

MP: 82-83 °C

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 2.51 (s, 3H), 6.84 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 1.7 Hz, 1H), 8.20 (dt, *J* = 2.1, 8.9 Hz, 2H), 8.25 (dt, *J* = 2.1, 9.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 30.1, 113.4, 123.5, 124.0, 128.8, 135.5, 142.8, 147.8, 153.2, 193.8.

HRMS: Calcd [M+1] for C₁₂H₉NO₅ calc: 232.0610; Found: 232.0617.

FTIR (film): 3460, 1675, 1511, 1352, 1291, 851, 769, 707 cm⁻¹.

MP: 160-161 °C

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.36 (t, *J* = 7.2 Hz, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 6.94 (d, *J* = 1.7 Hz, 1H), 7.57 (d, *J* = 1.7 Hz, 1H), 8.97 (t, *J* = 2.1 Hz, 1H), 9.32 (d, *J* = 2.1 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 14.2, 61.5, 114.12, 117.8, 118.3, 127.8, 132.8, 143.3, 148.5, 151.6, 162.7.

HRMS: Calcd [M+1] for C₁₃H₁₀N₂O₇: 307.0566; Found: 307.0577.

FTIR (film): 3421, 2366, 1721, 1644, 1542, 1347, 1296, 732 cm⁻¹.

MP: 93-94 °C

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.32 (t, *J* = 7.2 Hz, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 2.1 Hz, 1H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 14.2, 60.6, 113.1, 114.3, 123.6, 128.6, 129.8, 131.3, 141.3, 156.2, 163.4.

HRMS: Calcd [M+1] for C₁₃H₁₁BrO₃: 294.9970; Found: 294.9968.

FTIR (film): 3396, 2356, 1639, 1470, 1291, 1158, 1060, 1020 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

^1H NMR (400 MHz, CDCl_3): δ 1.23 (t, $J = 7.0$ Hz, 3H), 4.23 (q, $J = 7.2$ Hz, 2H), 6.89 (d, $J = 2.1$ Hz, 1H), 7.58 (d, $J = 7.0$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 13.9, 60.9, 106.2 (m), 111.9, 120.1, 138.1 (m), 139.0 (m), 142.5 (m), 143.8 (m), 144.6, 146.0 (m), 162.0.

HRMS: Calcd $[\text{M}+1]$ for $\text{C}_{13}\text{H}_7\text{O}_3\text{F}_3$: 307.0394; Found: 307.0399.

FTIR (film): 3426, 2925, 2858, 1926, 1654, 1608, 1506, 1445, 1194, 1076, 994, 743 cm^{-1} .

(^1H and ^{13}C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.34 (t, *J* = 7.2 Hz, 3H), 4.32 (q, *J* = 7.1 Hz, 2H), 6.89 (d, *J* = 1.7 Hz, 1H), 7.33 (m, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 8.36 (dt, *J* = 2.0, 8.0 Hz, 1H), 8.62 (dd, *J* = 1.4, 4.8 Hz, 1H), 9.12 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.5, 23.3, 25.2, 26.6, 30.8, 34.7, 47.5, 51.0, 65.1, 142.6, 150.9, 195.5, 200.7.

HRMS: Calcd [M+1] for 218.0817; Found: 218.0808.

FTIR (film): 3054, 2986, 2305, 1715, 1422, 1297, 1264, 1182, 1152, 1077, 895, 728 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.35 (t, *J* = 7.2 Hz, 3H), 4.31 (q, *J* = 7.2 Hz, 2H), 6.51 (dd, *J* = 1.7, 3.4 Hz, 1H), 6.78 (d, *J* = 1.7 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H), 7.50 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 14.3, 60.5, 111.8, 112.3, 112.7, 113.1, 141.0, 143.3, 144.5, 148.9, 162.8.

HRMS: Calcd [M+1] for C₁₁H₁₀O₄ calc: 207.0657; Found: 207.0647.

FTIR (film): 3416, 2966, 2361, 1726, 1654, 1301, 1188, 1148, 1065, 743 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.34 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.4 Hz, 3H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.37 (q, *J* = 7.3 Hz, 2H), 6.73 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 0.3, 1.75 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.1, 14.1, 61.5, 61.6, 112.9, 123.9, 143.9, 144.5, 157.8, 162.4.

HRMS: Calcd [M+1] for C₁₀H₁₂O₅ calc: 213.0763; Found: 213.0763.

FTIR (film): 3416, 2095, 1721, 1649, 1496, 1291, 1189, 1061, 758 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.32 (t, *J* = 7.2 Hz, 3H), 1.90 (dd, *J* = 1.7, 6.8 Hz, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 6.48 (dq, *J* = 7.0, 15.9 Hz, 1H), 6.64 (d, *J* = 2.1 Hz, 1H), 6.94 (dq, *J* = 1.7, 15.7 Hz, 1H), 7.19 (d, *J* = 2.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.3, 18.7, 60.2, 111.3, 112.2, 119.1, 130.9, 140.6, 156.9, 163.7.

HRMS: Calcd [M+1] for C₁₀H₁₂O₃ calc: 181.0865; Found: 181.0861.

FTIR (film): 2960, 1711, 1644, 1552, 1501, 1301, 1178, 1040, 978, 743 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.34 (t, *J* = 7.0 Hz, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.36 (q, *J* = 7.1, 2H), 6.54 (d, *J* = 16.1 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 1.8, Hz, 1H), 8.08 (d, *J* = 15.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.2, 14.2, 60.7, 61.0, 112.7, 119.4, 120.8, 129.6, 143.6, 153.4, 162.6, 166.4.

HRMS: Calcd [M+1] for C₁₂H₁₄O₅ calc: 239.0919; Found: 239.0911.

FTIR (film): 3402, 3367, 3054, 2988, 2304, 1711, 1422, 1265, 896, 740 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.30 (t, *J* = 7.2 Hz, 3H), 1.89 (d, *J* = 7.9 Hz, 6H), 4.20 (q, *J* = 7.2 Hz, 2H), 5.76 (d, *J* = 15.4, 1H), 5.99 (d, *J* = 12.7 Hz, 1H), 7.56 (dd, *J* = 11.6, 15.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.3, 18.9, 26.5, 60.1, 118.5, 123.7, 141.0, 146.2, 167.7.

HRMS: Calcd [M+1] for C₁₀H₁₄O₃ calc: 183.1021; Found: 183.1030.

FTIR (film): 3427, 2985, 2254, 1716, 1650, 1467, 1370, 1184, 908, 733, 650 cm⁻¹.

(¹H and ¹³C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.33 (t, *J* = 7.2 Hz, 3H), 1.98 (dd, *J* = 1.37, 6.8 Hz, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 6.37 (dq, *J* = 1.7, 15.7 Hz, 1H), 6.73 (d, *J* = 15.7 Hz, 1H), 7.05 (dq, *J* = 6.8, 15.7 Hz, 1H), 7.37 (d, *J* = 15.7 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.1, 18.6, 61.2, 130.9, 131.1, 137.9, 146.2, 165.6, 188.5.

HRMS: Calcd [M+1] for C₁₀H₁₂O₃ calc: 181.0865; Found: 181.0862.

FTIR (film): 3328, 3288, 3227, 3056, 2986, 2305, 2124, 1642, 1422, 1265, 895, 737 cm⁻¹.
(¹H and ¹³C NMR Spectra on following page)

^1H NMR (400 MHz, CDCl_3): δ 1.35 (d, $J = 6.8$ Hz, 6H), 1.39 (t, $J = 7.2$ Hz, 3H), 3.06 (m, 1H), 4.38 (q, $J = 7.1$ Hz, 2H), 6.56 (d, $J = 1.0$ Hz, 1H), 8.99 (t, $J = 2.1$ Hz, 1H), 9.33 (d, $J = 2.1$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 14.1, 20.8, 27.7, 61.3, 107.5, 117.7, 118.3, 127.3, 133.1, 148.4, 149.7, 163.0, 163.1.

HRMS: Calcd $[\text{M}+1]$ for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_7$ calc: 349.1036; Found: 349.1035.

FTIR (film): 3309, 3290, 3104, 3055, 2980, 2305, 1713, 1543, 1346, 1265, 1100, 1050, 910, 739 cm^{-1} .

MP: 122-123 $^\circ\text{C}$

(^1H and ^{13}C NMR Spectra on following page)

¹H NMR (400 MHz, CDCl₃): δ 1.39 (t, *J* = 7.2 Hz, 3H), 1.96 (dd, *J* = 1.7, 6.8 Hz, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 6.27 (dd, *J* = 1.7, 16.1 Hz, 1H), 6.47 (m, 1H), 6.65 (s, 1H), 8.99 (t, *J* = 2.1 Hz, 1H), 9.36 (d, *J* = 2.1 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 14.2, 18.5, 61.5, 109.2, 117.8, 118.3, 119.3, 127.4, 129.9, 132.9, 148.5, 149.5, 153.9, 162.8.

HRMS: Calcd [M+1] for C₁₆H₁₄N₂O₇ calc: 347.0879; Found: 347.0891.

FTIR (film): 3253, 3055, 2986, 2310, 1716, 1545, 1346, 1265, 1107, 1053, 896, 739 cm⁻¹.

MP: 130-132 °C

(¹H and ¹³C NMR Spectra on following page)

^1H NMR (300 MHz, CDCl_3): δ 1.28 (t, $J = 7.2$ Hz, 3H), 4.28 (q, $J = 7.1$ Hz, 2H), 6.97 (s, 1H), 7.08 (dd, $J = 3.6, 5.1$ Hz, 1H), 7.35 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 60.9, 105.9 (m), 106.0, 121.7, 124.5, 125.9, 127.8, 131.5, 136.3 (m), 138.8 (m), 140.9 (m), 140.9, 143.7 (m), 146.2 (m), 151.5, 161.7.

HRMS: Calcd $[\text{M}+1]$ for $\text{C}_{17}\text{H}_9\text{F}_5\text{O}_3\text{S}$: 389.0272; Found: 389.0271.

FTIR (film): 3945, 3693, 3055, 2986, 2686, 2360, 2307, 1723, 1659, 1579, 1519, 1502, 1445, 1422, 1385, 1321, 1265, 1245, 1217, 1143, 1099, 1053, 1012, 989, 897, 855, 792, 739, 706 cm^{-1}

MP: 68-71 $^\circ\text{C}$

(^1H and ^{13}C NMR Spectra on following page)

IV. The Isotopically Labeled Studies of Reductive Condensation of Propargylic Esters

High resolution mass spectra were obtained on a Micromass (Manchester, England) ZAB-E. All experiments were performed in tandem and were repeated 3-5 times. The spectra were averaged.

Calcd $[M+1]$ for $\text{C}_{13}\text{H}_{11}\text{NO}_6$: 278.0665
Calcd $[M+1]$ for $\text{C}_{13}\text{H}_{11}\text{NO}_5^{18}\text{O}$: 280.0707

$2.14 \pm 0.13 \%$

HRMS for ^{18}O -Enriched Compound, found $[M+1]$ for $\text{C}_{13}\text{H}_{11}\text{NO}_5^{18}\text{O}$: 280.0704

$7.01 \pm 0.31 \%$

Calcd [M+1] for $\text{C}_{13}\text{H}_{11}\text{NO}_5$: 262.0715
 Calcd [M+1] for $\text{C}_{13}\text{H}_{11}\text{NO}_4^{18}\text{O}$: 264.0758

HRMS for Result of ^{16}O -Compound

$1.93 \pm 0.12 \%$

HRMS for Result of ^{18}O -Enriched Compound, found [M+1] for $\text{C}_{13}\text{H}_{11}\text{NO}_4^{18}\text{O}$: 264.0763

$6.31 \pm 0.63 \%$

* O=PPh₃

Calcd [M+1] for C₁₈H₁₅OP: 279.0939

Calcd [M+1] for C₁₈H₁₅¹⁸OP: 281.0981

HRMS for Result of ¹⁶O-Compound

2.05 ± 0.11 %

HRMS for Result of ¹⁸O-Enriched Compound

2.18 ± 0.08 %