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Supporting Information

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Iridium Complex-Catalyzed Cross-Coupling Reaction of Terminal Alkynes with Internal Alkynes via C-H Activation of Terminal Alkynes

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Supporting Information

General Procedures. All starting materials were commercially available and used without any purification. The solvents were dried and purified before use by the usual procedures. ^1H and ^{13}C NMR spectra were measured at 270 and 67.5 MHz, respectively, in CDCl_3 with TMS as the internal standard. IR spectra were measured as films on NaCl plates. GLC analysis was performed with a flame ionization detector using a 1 mm $\times$ 30 m capillary column (OV-1). The conversions and yields of products were estimated from the peak areas based on the internal standard technique using GC.

Spectral Data

(*E*)-3-Phenyl-undec-2-en-4-ynoic acid methyl ester (3aa): ^1H NMR δ 7.63-7.60 (m, 2H), 7.30-7.28 (m, 3H), 6.42 (s, 1H), 3.71 (s, 3H), 2.51-2.46 (t, $J = 7.2$ Hz, 3H), 1.65-0.80 (m, 11H); ^{13}C NMR δ 165.8, 137.6, 129.6, 128.4, 127.1, 121.3, 105.2, 78.1, 51.4, 31.4, 28.8, 28.5, 22.6, 20.2, 14.1; IR (neat) 1722, 1224, 1114, 887 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 270.1620, Found: 270.1618.

(*E*)-5-(trimethylsilyl)-3-phenylpent-2-en-4-ynoic acid methyl ester (3ba): ^1H NMR δ 7.47-7.38 (m, 2H), 7.18-7.12 (m, 3H), 6.32 (s, 1H), 3.58 (s, 3H), 0.08 (s, 9H); ^{13}C NMR δ 165.7, 139.2, 134.2, 129.7, 129.0, 128.5, 127.2, 126.5, 123.4, 101.3, 78.5, 51.7, -0.30; IR (neat) 1730, 1251, 1167, 846 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 258.1076, Found:

258.1082.

(E)-3,5-diphenylpent-2-en-4-ynoic acid methyl ester (3ca): ^1H NMR δ 7.80-7.36 (m, 10H), 6.59 (s, 1H), 3.84 (s, 3H); ^{13}C NMR δ 165.6, 136.9, 136.6, 132.0, 129.9, 129.2, 128.6, 128.3, 127.1, 122.6, 122.1, 102.2, 86.8, 51.6; IR (neat) 1777, 1322, 1178, 876, 722 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 262.0994, Found: 262.0998.

(E)-4-deuterio-3,5-diphenylpent-2-en-4-ynoic acid methyl ester (3ca- d_1): ^1H NMR δ 7.80-7.36 (m, 10H), 3.84 (s, 3H); ^{13}C NMR δ 165.6, 136.9, 136.6, 132.0, 129.9, 129.2, 128.6, 128.3, 127.1, 122.6, 122.1, 102.2, 86.8, 51.6.

(E)-6-tert-butoxy-3-phenylhept-2-en-4-ynoic acid methyl ester (3da): ^1H NMR δ 7.60-7.33 (m, 5H), 6.28 (s, 1H), 4.29 (s, 1H), 3.69 (s, 3H), 1.43-1.41 (d, $J = 6.7$ Hz, 3H), 1.26 (s, 9H); ^{13}C NMR δ 167.9, 167.8, 166.1, 165.4, 143.2, 137.1, 134.1, 133.3, 130.0, 130.0, 53.5, 53.3, 53.1, 33.6, 33.5, 22.9, 14.2; IR (neat) 2977, 1740, 1450, 843 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 287.1647, Found: 287.1632.

(E)-5-(1-hydroxycyclohexyl)-3-phenylpent-2-en-4-ynoic acid methyl ester (3ea): ^1H NMR δ 7.71-7.67 (m, 2H), 7.38-7.35 (m, 3H), 6.51 (s, 1H), 3.75 (s, 3H), 2.13-1.21 (m, 10H); ^{13}C NMR δ 165.5, 136.7, 136.5, 129.8, 126.9, 125.5, 121.8, 107.0, 81.1, 69.0, 51.5, 39.6, 25.2, 23.2; IR (neat) 3475, 2948, 1722, 1258, 1160, 829 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 284.1412, Found: 284.1420.

(E)-3-pentylundec-2-en-4-ynoic acid methyl ester (3ab-(E)): ^1H NMR δ 6.18 (s, 1H), 3.84 (s, 3H), 2.08-0.96 (m, 24H); ^{13}C NMR δ 166.5, 145.1, 127.6, 92.1, 86.8, 53.0, 31.4, 30.6, 29.6, 28.4, 26.5, 24.4, 22.4, 21.2, 18.8, 16.4, 15.2; IR (neat) 2748, 1740, 1352, 1098, 822 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 264.2089, Found: 264.2094.

(Z)-3-pentylundec-2-en-4-ynoic acid methyl ester (3ab-(Z)): ^1H NMR δ 5.92 (s, 1H), 3.86 (s, 3H), 2.21-0.97 (m, 24H); ^{13}C NMR δ 165.4, 140.2, 127.9, 102.1, 82.4, 53.2, 31.4, 30.8, 29.6, 28.2, 26.4, 24.4, 22.4, 21.6, 19.2, 17.0, 15.1; IR (neat) 2749, 1738, 1340, 1120, 845 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 264.2089, Found: 264.2080.

(E)-3-Pentyl-5-phenyl-pent-2-en-4-ynoic acid methyl ester (3cb-(E)): ^1H NMR δ 7.56-7.32 (m, 5H), 6.02 (s, 1H), 3.76 (s, 3H), 2.39-2.33 (t, $J = 7.3$ Hz 2H), 1.72-1.31 (m, 6H), 0.93-0.88 (t, $J = 6.7$ Hz 3H); ^{13}C NMR δ 165.6, 140.0, 132.1, 129.0, 128.3, 123.2, 122.7, 100.8, 87.6, 51.3, 38.7, 31.0, 27.7, 22.4, 13.9; IR (neat) 2822, 1744, 1282, 1089, 928 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 256.1463, Found: 256.1458.

(Z)-3-Pentyl-5-phenyl-pent-2-en-4-ynoic acid methyl ester (3cb-(Z)): ^1H NMR δ 7.55-7.32 (m, 5H), 5.98 (s, 1H), 3.78 (s, 3H), 2.44-2.39 (t, $J = 7.3$ Hz 2H), 1.81-1.46 (m, 6H), 0.94-0.89 (t, $J = 6.7$ Hz 3H); ^{13}C NMR δ 164.8, 138.6, 131.9, 129.1, 128.4, 123.1, 122.0, 104.2, 84.2, 51.2, 38.8, 30.1, 27.6, 22.4, 13.6; IR (neat) 2842, 1748, 1288, 1090, 922 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 256.1463, Found: 256.1470.

(E)-6-tert-Butoxy-3-pentyl-hept-2-en-4-ynoic acid methyl ester (3dc-(E)): ^1H NMR δ 5.99 (s, 1H), 4.46-4.38 (q, $J = 6.7$ Hz, 1H), 3.69 (s, 3H), 2.75-2.69 (t, $J = 7.3$ Hz, 2H), 1.58-0.86 (m, 21H); ^{13}C NMR δ 166.1, 143.4, 122.9, 97.8, 84.1, 74.8, 58.0, 51.2, 32.2, 31.4, 28.2, 28.1, 24.1, 22.6, 14.1; IR (neat) 2986, 1758, 1422, 820 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 280.2039, Found: 280.2026.

(Z)-6-tert-Butoxy-3-pentyl-hept-2-en-4-ynoic acid methyl ester (3dc-(Z)): ^1H NMR δ 5.93 (s, 1H), 4.57-4.49 (q, $J = 6.7$ Hz, 1H), 3.72 (s, 3H), 2.28-2.22 (t, $J = 7.3$ Hz, 2H), 1.63-0.86 (m, 21H); ^{13}C NMR δ 165.3, 139.8, 122.8, 104.5, 81.2, 74.7, 58.2, 51.2, 38.9, 31.0, 28.2, 27.6, 24.1, 22.5, 14.0; IR (neat) 2980, 1762, 1421, 836 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 280.2039, Found: 280.2033.

6-tert-Butoxy-3-pentyl-hept-2-en-4-ynal (3dd): ^1H NMR δ 9.99 (s, 1H), 6.10 (s, 1H), 4.52-4.45 (q, $J = 6.7$ Hz 1H), 2.35-2.30 (t, $J = 7.3$ Hz 2H), 1.66-0.87 (m, 21H); ^{13}C NMR δ 192.8, 147.2, 134.2, 104.4, 79.4, 75.0, 58.0, 38.4, 31.1, 28.2, 27.3, 24.1, 22.4, 14.0; IR (neat) 2866, 1772, 1755, 1421, cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 250.1933, Found: 250.1922.

3-(3-tert-Butoxy-but-1-ynyl)-oct-3-enal (5dd): ^1H NMR δ 10.01 (s, 1H), 5.68 (t, $J = 7.3$ Hz 1H), 4.42-4.35 (q, $J = 6.7$ Hz 1H), 3.11 (s, 1H), 2.01-1.96 (m, 1H), 1.66-0.87 (m, 21H); ^{13}C NMR δ 198.6, 136.1, 120.1, 102.8, 78.9, 74.1, 59.6, 50.2, 36.4, 30.2, 28.2, 27.4, 25.5, 22.2, 13.9; IR (neat) 2865, 1782, 1746, 1389, cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 250.1933, Found: 250.1940.

(E)-1,2-Diphenyl-nona-1-en-3-yne (3ae): ^1H NMR δ 7.36-7.08 (m, 10H), 6.98 (s, 1H), 2.42-2.35 (t, $J = 7.2$ Hz, 2H), 1.62-0.88 (m, 11H); ^{13}C NMR δ 138.2, 136.3, 135.1, 129.3, 128.9, 128.2, 128.1, 127.1, 126.8, 124.8, 91.6, 83.8, 31.1, 22.0, 19.2, 14.1; IR (neat) 3011, 2248, 1601, 1498, 911 cm^{-1} ; HRMS (CI, M^+) m/z Calcd for 288.1878, Found: 288.1877.