Supporting Information for

Catalytic and Highly Efficient 1,4-Addition of Terminal Alkynes to Conjugated Enones by $[RuCl_2(p\text{-cymene})]_2$/pyrrolidine

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6-Trimethylsilyl-5-hexyne-2-one (entry 2 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 2.68 (2H, t, *J* = 6.4 Hz), 2.48 (2H, t, *J* = 6.4 Hz), 2.17 (3H, s), 0.14 (9H, s); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 206.7, 106.0, 85.4, 42.8, 30.2, 14.8, 0.4; IR (neat) cm^{-1} 2380, 2178, 1721, 843; HRMS (EI) calcd for $C_9H_{16}SiO$ [M^+] 168.0971, found 168.0963.

10-Hydroxy-5-decyne-2-one (entry 3 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 3.67 (2H, t, *J* = 6.1 Hz), 2.64 (2H, t, *J* = 6.7 Hz), 2.41 (2H, m), 2.17 (5H, m), 1.69-1.49 (5H, m); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.9, 80.9, 79.1, 62.4, 43.2, 32.1, 30.1, 25.5, 18.8, 13.7; IR (neat) cm^{-1} 3412, 2935, 2420, 1718, 1365, 1164, 1058; HRMS (EI) calcd for $C_{10}H_{16}O_2$ [M^+] 168.1151, found 168.1153.

7,7-Dimethyl-5-octyne-2-one (entry 4 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 2.62 (2H, t, *J* = 6.7 Hz), 2.40 (2H, t, *J* = 7.6 Hz), 2.17(3H, s), 1.18 (9H, s); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.4, 89.9, 77.2, 43.5, 31.6, 30.4, 27.6, 13.9; IR (neat) cm^{-1} 2969, 2442, 1719, 1362; HRMS (EI) calcd for $C_{10}H_{16}O$ [M^+] 152.1202, found 152.1199.

9-Oxo-5-decynonitrile (entry 5 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 2.65 (2H, t, *J* = 6.9 Hz), 2.48 (2H, t, *J* = 6.9 Hz), 2.44-2.30 (4H, m), 2.18 (3H, s), 1.82 (2H, m); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.3, 119.7, 81.2, 78.1, 43.0, 30.3, 25.1, 18.2, 16.4, 13.6; IR (neat) cm^{-1} 2338, 2248, 1712, 1637; MS (EI) calcd for $C_{10}H_{13}NO$ [M^+] 163.0982, found 163.0998.

9-Chloro-5-nonyne-2-one (entry 6 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 3.65 (2H, t, *J* = 6.4 Hz), 2.64 (2H, m, *J* = 6.6 Hz), 2.44-2.30 (4H, m), 2.17 (3H, s), 1.91 (2H, m); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.3, 80.1, 79.1, 44.1, 43.2, 32.0, 30.3, 16.5, 13.7; IR (neat) cm^{-1} 2922, 2442, 1719, 1434, 1163, 650; HRMS (CI) calcd for $C_9H_{13}ClO$ [M^+] 172.0656, found 172.0659.

(2-Oxo-5-nonynyl)-4-pentenoate (entry 7 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 5.84 (1H, m), 5.05 (2H, m), 4.19 (2H, t, *J* = 6.3 Hz), 2.64 (2H, t, *J* = 6.3 Hz), 2.43-2.37 (6H, m), 2.26-2.19 (2H, m), 2.17 (3H, s), 1.80-1.72 (2H, m); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.3, 173.4, 137.0, 115.9, 79.8, 79.5, 63.5, 43.2, 33.9, 30.3, 29.3, 28.3, 15.8, 13.7; IR (neat) cm^{-1} 2959, 2347, 1719, 1167, 916; HRMS (CI) calcd for $C_{14}H_{20}O_3$ [M^+] 236.1413, found 236.1422.

6-(4-Methylphenyl)-5-hexyne-2-one (entry 8 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 7.27 (2H, d, *J* = 8.1 Hz), 7.08 (2H, d, *J* = 8.1 Hz), 2.75-2.65 (4H, m), 2.33 (3H, s), 2.20 (3H, s); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.0, 138.1, 131.8, 129.4, 120.9, 88.1, 81.4, 43.0, 30.3, 21.8, 14.4; IR (neat) cm^{-1} 2923, 2232, 1719, 1430, 1412, 1364; HRMS

(EI) calcd for $C_{13}H_{14}O$ [M^+] 184.1046, found 186.1036.

5,11-Hexadecadiyne-2,15-dione (entry 9 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 2.63 (4H, t, *J* = 7.0 Hz), 2.41 (4H, m), 2.18 (6H, s), 2.17-2.13 (4H, m), 1.54 (4H, m); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.5, 80.8, 79.2, 43.3, 30.3, 28.4, 18.6, 13.8; IR (neat) cm^{-1} 2929, 1717, 1432, 1364, 1163; HRMS (EI) calcd for $C_{16}H_{22}O_2$ [M^+] 246.1621, found 246.1612.

(1-Cyclohexenyl)-5-hexyn-2-one (entry 10 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 6.00 (1H, bs), 2.72 (2H, t, *J* = 7.6 Hz), 2.54 (2H, t, *J* = 7.6 Hz), 2.18 (3H, s), 2.06 (4H, m), 1.58 (4H, m); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 207.3, 134.2, 121.1, 85.9, 83.2, 43.2, 30.3, 29.8, 25.9, 22.7, 21.9, 14.3; IR (neat) cm^{-1} 2930, 2216, 1717, 1434, 1362, 1163; HRMS (EI) calcd for $C_{12}H_{16}O$ [M^+] 176.1202, found 176.1207.

10-Chloro-6-decyne-3-one (entry 11 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 3.63 (2H, t, *J* = 6.3 Hz), 2.61 (2H, t, *J* = 7.1 Hz), 2.50-2.30 (6H, m), 1.91 (2H, m), 1.07 (3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 210.1, 80.3, 79.0, 44.2, 41.9, 36.4, 31.9, 16.5, 13.8, 8.1; IR (neat) cm^{-1} 2939, 2381, 1711, 1457, 1414, 1114, 651; HRMS (EI) calcd for $C_{10}H_{15}ClO$ [M^+] 186.0813, found 186.0815.

6-Pentadecyne-3-one (entry 12 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 2.64 (2H, t, *J* = 6.5 Hz), 2.44 (4H, m), 2.11 (2H, m), 1.45-1.09 (12H, m), 1.07 (3H, t, *J* = 6.9 Hz), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 210.2, 81.3, 78.9, 42.1, 36.4, 32.2, 29.6, 29.5, 29.4, 29.3, 23.1, 19.1, 14.5, 13.9, 8.1; IR (neat) cm^{-1} 2930, 2858, 1719,

1461, 1365, 1113, 972, 723; HRMS (EI) calcd for $C_{15}H_{26}O$ [M^+] 222.1985, found 222.1996.

(7-Chloro-3-heptynyl) phenyl ketone (entry 13 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 7.99-7.96 (2H, m), 7.55 (1H, m), 7.49-7.44 (2H, m), 3.62 (2H, t, J = 6.4 Hz), 3.18 (2H, t, J = 6.4 Hz), 2.59 (2H, m), 2.31 (2H, m), 1.88 (2H, m); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 198.6, 137.1, 133.6, 129.0, 128.4, 80.4, 79.2, 44.2, 38.5, 32.0, 16.6, 14.1; IR (neat) cm^{-1} 2916, 2400, 1681, 1447, 690; HRMS (EI) calcd for $C_{14}H_{15}ClO$ [M^+] 234.0813, found 234.0817.

3-Dodecynyl phenyl ketone (entry 14 in Table 2): ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 7.99-7.96 (2H, m), 7.55 (1H, m), 7.49-7.43 (2H, m), 3.19 (2H, t, J = 8.9 Hz), 2.59 (2H, m), 2.12 (2H, m), 1.48-1.43 (2H, m), 1.32-1.26 (10H, m), 0.88 (2H, t, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 197.3, 135.7, 132.1, 127.6, 127.0, 80.0, 77.7, 37.3, 30.8, 28.7, 28.2, 28.0, 27.9, 21.6, 17.7, 13.1, 12.8; IR (neat) cm^{-1} 2927, 2360, 1688, 1450, 1205, 742, 690; HRMS (EI) calcd for $C_{19}H_{26}O$ [M^+] 270.1985, found 270.1985.

A new complex of [(*p*-cymene)$RuCl_2$(pyrrolidine)] was formed at room temperature immediately after addition of 2.0 equiv of pyrrolidine to a solution of 1.0 equiv of [$RuCl_2$(*p*-cymene)]$_2$ in C_6D_6: ^{1}H NMR (C_6D_6, 250 MHz) δ 4.78 (2H, d, J_{AB} = 6.1 Hz), 4.71 (2H, d, J_{AB} = 6.1 Hz), 3.57 (2H, m), 3.07 (1H, septet, J = 6.9 Hz), 2.29 (2H, m), 2.00 (3H, s), 1.38 (4H, m), 1.22 (6H, d, J = 6.9 Hz). {[$RuCl_2$(*p*-cymene)]$_2$}: ^{1}H NMR (C_6D_6, 250 MHz) δ 5.10 (2H, d, J_{AB} = 5.9 Hz), 4.92 (2H, d, J_{AB} = 5.9 Hz), 2.96 (1H, septet, J = 6.9 Hz), 1.95 (3H, s), 1.16 (6H, d, J = 6.9 Hz).