

Palladium(II)-Catalyzed Three-Component Coupling Reaction Initiated by Acetoxypalladation of Alkynes: An Efficient Route to γ , δ -Unsaturated Carbonyls

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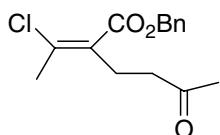
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Supporting Information

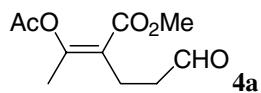
Typical Procedure for the Coupling Reaction of **1a** and Acrolein (Table 1, entry 1):

To a solution of Pd(OAc)₂ (5.6 mg, 0.025 mmol) and 2,2'-bipyridine (4.7 mg, 0.030 mmol) in HOAc (1 mL) and MeCN (3 mL) at 80 °C was added **1a** (98 mg, 1 mmol) and acrolein (0.67 mL, 10 mmol) with stirring. The reaction mixture was monitored by TLC. After the reaction was complete, ethyl ether (20 mL) was added. On cooling, the reaction mixture was neutralized with saturated NaHCO₃, then extracted with Et₂O. The combined ether solution was washed with saturated NaCl, dried (Na₂SO₄) and concentrated. The residue was purified by flash chromatography (EtOAc: petroleum ether = 1: 4) to give the coupling products in 72 % yield (**4a** : **5a** > 97 : 3).



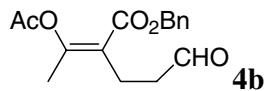
(Z)-6-Chloro-5-benzyloxycarbonylhept-5-en-2-one

Oil. ^1H NMR (300 MHz, CDCl_3): δ 7.47-7.30 (m, 5H), 5.23 (s, 2H), 2.66-2.48 (m, 4H), 2.21 (s, 3H), 2.08 (s, 3H); IR (neat): ν 2920, 1730, 1420, 1370, 1285, 1160, 1080, 1015, 750, 700 cm^{-1} ; MS (EI): m/z : 283 [$\text{M}^+({}^{37}\text{Cl})+1$], 281 [$\text{M}^+({}^{35}\text{Cl})+1$], 245, 222, 173, 129, 104, 91 (100), 77, 65, 43; HRMS Calcd for $\text{C}_{15}\text{H}_{17}\text{ClO}_3$ [$\text{M}^+({}^{35}\text{Cl})$] 280.0866, found 280.0908.



(Z)-5-Acetoxy-4-methoxycarbonylhex-4-enal

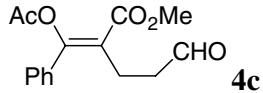
Oil. ^1H NMR (300 MHz, CDCl_3): δ 9.73 (s, 1H), 3.65 (s, 3H), 2.59-2.56 (m, 4H), 2.17 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 201.0, 168.7, 165.9, 154.4, 118.8, 51.82, 43.0, 21.5, 20.9, 18.6; IR (neat): ν 2955, 2732, 1762, 1723, 1655, 1372, 1231, 1172, 1090, 1016 cm^{-1} ; MS (EI): m/z : (M^++1), 215, 173, 155, 154 ($\text{M}^+ - \text{HOAc}$), 129, 116, 97, 43 (100). HRMS Calcd for $\text{C}_8\text{H}_{10}\text{O}_3$ [$\text{M}^+ - \text{HOAc}$] 154.0630, found 154.0616.



(Z)-5-Acetoxy-4-benzyloxycarbonylhex-4-enal

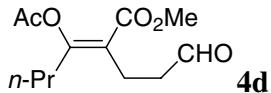
Oil. ^1H NMR (300 MHz, CDCl_3): δ 9.77 (s, 1H), 7.38-7.27 (m, 5H), 5.15 (s, 2H), 2.65 (s, 4H), 2.04 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 200.9, 168.6, 165.4, 154.4, 135.5, 128.6, 128.4, 128.3, 118.9, 66.7, 42.9, 21.5, 20.5, 18.6; IR (neat): ν 3036, 2956, 2729, 1760, 1721, 1654, 1499, 1456, 1226, 1168, 1015, 1081, 755, 700 cm^{-1} ; MS (EI): m/z : 291 (M^++1), 230 ($\text{M}^+ - \text{HOAc}$), 139, 141, 92, 91(100), 77, 65, 43; HRMS

Calcd for C₁₄H₁₄O₃ [M⁺-HOAc] 230.0943, found 230.0905.



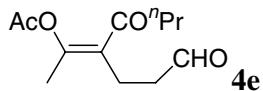
(Z)-5-Acetoxy-4-methoxycarbonyl-5-phenylpent-4-enal

Oil. ¹H NMR (300 MHz, CDCl₃): δ 9.68 (s, 1H), 7.41-7.39 (m, 5H), 3.79 (s, 3H), 2.67-2.62 (m, 4H), 2.16 (s, 3H); IR (neat): ν 2954, 2841, 2730, 1765, 1722, 1648, 1492, 1436, 1370, 1326, 1207, 890, 701 cm⁻¹; MS (EI): *m/z*: 277 (M⁺+1), 233, 217(100), 216 (M⁺-HOAc), 105, 43; HRMS Calcd for C₁₄H₁₂O₃ [M⁺-HOAc] 216.0786, found 216.0794.



(Z)-5-Acetoxy-4-methoxycarbonyloct-4-enal

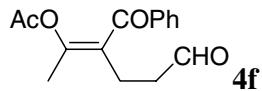
Oil. ¹H NMR (300 MHz, CDCl₃): δ 9.80 (s, 1H), 3.71 (s, 3H), 2.65 (s, 4H), 2.34 (t, *J* = 7.56 Hz, 2H), 2.05 (s, 3H), 1.54 (dt, *J* = 7.56 Hz, *J* = 7.49 Hz, 2H), 0.96 (t, *J* = 7.49 Hz, 3H); IR (neat): ν 2966, 2729, 1763, 1723, 1647, 1436, 1370, 1236, 1222, 1168, 1099, 1060, 929 cm⁻¹; MS (EI): *m/z*: 182 (M⁺-HOAc), 169, 157, 144, 125, 116, 71, 43(100); HRMS Calcd for C₁₀H₁₄O₃ [M⁺-HOAc] 182.0943, found, 182.0920.



(Z)-5-Acetoxy-4-butyrylhex-4-enal

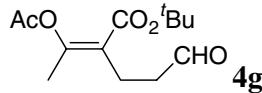
Oil. ¹H NMR (300 MHz, CDCl₃): δ 9.77 (s, 1H), 2.60-2.51 (m, 4H), 2.19 (s, 3H), 2.05

(s, 3H), 1.64-1.59 (m, 4H), 0.97-0.89 (m, 3H); IR (neat): ν 2966, 2877, 2729, 1761, 1724, 1665, 1459, 1372, 1018, 898 cm^{-1} ; MS (EI): m/z : 227 (M^++1), 166 ($M^+-\text{HOAc}$), 141, 128, 100, 71, 43(100); HRMS Calcd for $C_{10}\text{H}_{14}\text{O}_2$ [$M^+-\text{HOAc}$] 166.0904, found 166.0985.



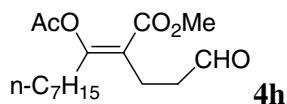
(Z)-5-Acetoxy-4-benzoylhex-4-enal

Oil. ^1H NMR (300 MHz, CDCl_3): δ 9.79 (s, 1H), 7.79-7.76 (m, 2H), 7.53-7.52 (m, 1H), 7.47-7.40 (m, 2H), 2.70-2.68 (m, 4H), 2.16 (s, 3H), 1.51 (s, 3H); IR (neat): ν 3063, 2831, 2731, 1757, 1724, 1660, 1598, 1580, 1449 cm^{-1} ; MS (EI): m/z : 200 ($M^+-\text{HOAc}$), 199, 105, 162, 97, 43(100); HRMS Calcd for $C_{13}\text{H}_{12}\text{O}_2$ [$M^+-\text{HOAc}$] 200.0837, found 200.0804.



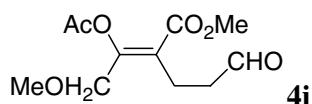
(Z)-5-Acetoxy-4-tert-butoxycarbonylhex-4-enal

Oil. ^1H NMR (300 MHz, CDCl_3): δ 9.80 (s, 1H), 2.66-2.56 (m, 4H), 2.16 (s, 3H), 1.99 (s, 3H), 1.46 (s, 9H); IR (neat): ν 2980, 2729, 1762, 1717, 1658, 1370, 1233, 1153, 1087, 849 cm^{-1} ; MS (EI): m/z : 257 (M^++1), 201(100), 183 ($M^+-\text{O}'\text{Bu}$), 141, 43, 41; HRMS Calcd for $C_9\text{H}_{11}\text{O}_4$ [$M^+-\text{O}'\text{Bu}$] 183.0657, found 183.0661.



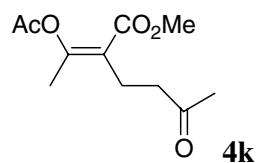
(Z)-5-Acetoxy-4-methoxycarbonyldodec-4-enal

Oil. ^1H NMR (300 MHz, CDCl_3): δ 9.80 (s, 1H), 3.71 (s, 3H), 2.65 (s, 4H), 2.35 (t, $J = 7.4\text{Hz}$ 2H), 2.19 (s, 3H), 1.49-1.46 (m, 2H), 1.33-1.28 (m, 8H), 0.88 (t, $J = 6.4\text{ Hz}$, 3H); IR (neat): ν 2965, 2858, 2726, 1764, 1723, 1646, 1460, 1436, 1369, 1227, 1167, 1102, 923 cm^{-1} ; MS (EI): m/z : 266, 238 ($\text{M}^+ \text{-HOAc}$), 254(100), 225, 213, 41; HRMS Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3$ [$\text{M}^+ \text{-HOAc}$] 238.1569, found 238.1591.



(Z)-5-Acetoxy-4-methoxycarbonyl-6-methoxyhex-4-enal

Oil. ^1H NMR (300 MHz, CDCl_3): δ 9.91 (s, 1H), 4.28 (s, 2H), 3.87 (s, 4H), 3.48 (s, 3H), 2.81 (s, 3H), 2.00 (s, 3H); IR (neat): ν 2954, 2829, 2733, 1764, 1724, 1655, 1437, 1371, 1319, 1226, 1171, 1084, 922 cm^{-1} ; MS (EI): m/z : 245 ($\text{M}^+ + 1$), 185 ($\text{M}^+ \text{-OAc}$), 171, 152, 142, 125, 127, 43(100); HRMS Calcd for $\text{C}_9\text{H}_{13}\text{O}_4$ [$\text{M}^+ \text{-OAc}$] 185.0814, found 185.0768.



(Z)-6-Acetoxy-5-methoxycarbonylhept-5-en-2-one

Oil. ^1H NMR (300 MHz, CDCl_3): δ 3.72 (s, 3H), 2.65-2.55 (m, 4H), 2.17 (s, 3H), 2.16 (s, 3H), 2.04 (s, 3H); IR (neat): ν 2955, 1762, 1720, 1656, 1437, 1369, 1230, 1167

cm^{-1} ; MS (EI): m/z : 197, 187, 168 ($\text{M}^+ \text{-HOAc}$), 155, 129, 97, 43(100); HRMS Calcd for $\text{C}_9\text{H}_{12}\text{O}_3$ [$\text{M}^+ \text{-HOAc}$] 168.0786, found 168.0780.

