Supporting Information
for
Pd(0)-Catalyzed Coupling-Cyclization of 2-(2',3'-Allenyl)acetylacetates
and Organic Halides: An Efficient Synthesis of 4,5-Dihydrofuran
Derivatives

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General Procedure :

$K_3PO_4 \cdot 3H_2O$ (80 mg, 0.3 mmol) was dried in a reaction tube. Then $Pd(PPh_3)_4$ (9 mg, 0.008 mmol, 5 mol%), 2 mL of dry DMF, 2-(2',3'-allenyl)acetylacetate **1** (0.15 mmol), and RI (0.18 mmol, 1.2 equiv.) were added sequentially. The reaction mixture was refluxed under N_2 or Ar. After the reaction was complete as monitored by TLC (petroleum ether : ethyl acetate = 5 : 1), it was quenched with water, extracted with ethyl ether, and dried over Na_2SO_4 . Filtration, rotary evaporation and flash chromatography on silica gel (eluent : petroleum ether : ethyl ether = 8 : 1) afforded the product **3**.

The following compounds were prepared according to **General Procedure** :

(1) 2-Methyl-5-(1-phenylvinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (**3aa**)

The reaction of **1a** (28 mg, 0.15 mmol), PhI (37 mg, 0.18 mmol), $Pd(PPh_3)_4$ (9 mg, 0.008 mmol), and $K_3PO_4 \cdot 3H_2O$ (80 mg, 0.3 mmol) in DMF (2 mL) afforded 40 mg (100 %) of **3aa**. Liquid; 1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5 H), 5.53 (dd, J = 10.2, 8.4 Hz, 1 H), 5.43 (s, 1 H), 5.35 (s, 1 H), 4.14 (q, J = 6.9 Hz, 2 H), 3.12 (ddq, J = 14.4, 11.1, 1.5 Hz, 1 H), 2.68 (ddq, J = 14.4, 8.4, 1.5 Hz, 1 H), 2.28 (t, J = 1.5 Hz, 3 H), 1.24 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 167.5, 166.0, 147.2, 138.2, 128.5, 127.9, 126.6, 112.4, 101.8, 82.2, 59.5, 36.0, 14.4, 14.1; MS (EI) m/z (%) 259 ($M+H^+$, 1.80), 258 (M^+ , 0.57), 43 (100); IR (neat) 3057, 2979, 2928, 1699, 1652, 1384, 1226,

1084 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_3$ ($\text{M}+\text{H}^+$) 259.1329. Found 259.1335.

(2) 2-Methyl-5-(1-*p*-tolylvinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3ab)

The reaction of **1a** (46 mg, 0.25 mmol), *p*-MeC₄H₉I (64 mg, 0.29 mmol), $\text{Pd(PPh}_3)_4$ (16 mg, 0.014 mmol), and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (80 mg, 0.3 mmol) in DMF (2 mL) afforded 60 mg (87 %) of **3ab**. Liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.27 (d, $J = 6.6$ Hz, 2 H), 7.16 (d, $J = 8.1$ Hz, 2 H), 5.52 (dd, $J = 10.8, 8.4$ Hz, 1H), 5.40 (s, 1 H), 5.31 (t, $J = 1.2$ Hz, 1 H), 4.14 (dq, $J = 7.2, 1.2$ Hz, 2 H), 3.12 (ddq, $J = 14.4, 10.8, 1.5$ Hz, 1H), 2.68 (ddq, $J = 14.4, 8.1, 1.5$ Hz, 1 H), 2.36 (s, 3 H), 2.29 (t, $J = 1.5$ Hz, 3 H), 1.25 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 167.5, 166.0, 147.0, 137.7, 135.2, 129.1, 126.4, 111.5, 101.7, 82.2, 59.4, 36.0, 21.0, 14.3, 14.0; MS (EI) m/z (%) 272 (M^+ , 0.62), 43 (100); IR (neat) 2926, 2869, 1699, 1651, 1514, 1383, 1227, 1083 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$ (M^+) 272.1412. Found 272.1399.

(3) 2-Methyl-5-(1-(*p*-methoxyphenyl)vinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3ac)

The reaction of **1a** (45 mg, 0.25 mmol), *p*-MeOC₄H₉I (72 mg, 0.31 mmol), Pd(PPh₃)₄ (16 mg, 0.014 mmol), and K₃PO₄·3H₂O (80 mg, 0.3 mmol) in DMF (2 mL) afforded 63 mg (89 %) of **3ac**. Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.25 (m, 2 H), 6.90-6.83 (m, 2 H), 5.50 (dd, *J* = 10.8, 8.4 Hz, 1 H), 5.35 (s, 1 H), 5.26 (s, 1 H), (q, *J* = 6.9 Hz, 2 H), 3.80 (s, 3 H), 3.11 (ddq, *J* = 14.4, 10.8, 1.5 Hz, 1 H), 2.66 (ddq, *J* = 14.4, 8.4, 1.5 Hz, 1 H), 2.28 (t, *J* = 1.5 Hz, 3 H), 1.24 (t, *J* = 6.9 Hz, 3 H), ¹³C NMR (CDCl₃, 75.4 MHz) δ 167.5, 166.0, 159.3, 146.5, 130.5, 127.7, 113.8, 110.9, 101.7, 82.4, 59.4, 55.2, 36.0, 14.3, 14.0; MS (EI) *m/z* (%) 288 (M⁺, 4.64), 43 (100); IR (neat) 2979, 2935, 1697, 1651, 1608, 1513, 1384, 1249, 1226, 1084; HRMS (EI) calcd for C₁₇H₂₀O₄ (M⁺) 288.1362. Found 288.1360.

(4) 2-Methyl-5-(1-(*p*-(methoxycarbonyl)phenyl)vinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3ad**)**

The reaction of **1a** (45 mg, 0.25 mmol), *p*-MeO₂CC₄H₉I (79 mg, 0.30 mmol),

Pd(PPh₃)₄ (15 mg, 0.014 mmol), and K₃PO₄·3H₂O (82 mg, 0.3 mmol) in DMF (2 mL) afforded 43 mg (58 %) of **3ad**. Liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.00 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.4, 2 H), 5.55-5.48 (m, 2 H), 5.43 (s, 1 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 3.91 (s, 3 H), 3.12 (t, *J* = 12.9 Hz, 1 H), 2.64 (dd, *J* = 14.4, 8.4 Hz, 1 H), 2.26 (s, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 167.4, 166.7, 165.9, 146.4, 142.6, 129.7, 129.5, 126.6, 114.3, 101.8, 81.8, 59.5, 52.1, 35.9, 14.3, 14.0; MS (EI) *m/z* (%) 316 (M⁺, 0.55), 43 (100); IR (neat) 2980, 2952, 1724, 1700, 1653, 1609, 1436, 1385, 1282, 1226, 1113, 1083; HRMS (MALDI/DHB) calcd for C₁₈H₂₀O₅Na (M+Na⁺) 339.1203. Found 339.1203.

(5) 2-Methyl-5-(1-(*p*-acetylphenyl)vinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3ae)

The reaction of **1a** (27 mg, 0.15 mmol), *p*-MeOCC₄H₉I (45 mg, 0.18 mmol), Pd(PPh₃)₄ (9 mg, 0.008 mmol), and K₃PO₄·3H₂O (81 mg, 0.3 mmol) in DMF (2 mL) afforded 46 mg (100 %) of **3ae**. Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 5.56-5.48 (m, 2 H), 5.44 (s, 1 H), 4.12 (dq, *J* = 7.2, 1.2 Hz, 2 H), 3.12 (ddq, *J* = 14.4, 10.8, 1.5 Hz, 1 H), 2.64 (ddq, *J* = 14.4, 8.4, 1.5 Hz, 1 H), 2.60 (s, 3 H), 2.26 (t, *J* = 1.5 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 197.5, 167.4, 165.9, 146.4, 142.8, 136.3, 128.5, 126.8, 114.6, 101.8, 81.9,

59.5, 35.9, 26.6, 14.3, 14.0; MS (EI) m/z (%) 300 (M^+ , 0.58), 43 (100); IR (neat) 2980, 2927, 1686, 1654, 1605, 1384, 1267, 1226, 1085; HRMS (MALDI/DHB) calcd for $C_{18}H_{20}O_4Na$ ($M+Na^+$) 323.1254. Found 323.1255.

(6) 2-Methyl-5-(1-(*p*-bromophenyl)vinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3af)

The reaction of **1a** (45 mg, 0.25 mmol), *p*-BrC₄H₉I (85 mg, 0.30 mmol), $Pd(PPh_3)_4$ (16 mg, 0.014 mmol), and $K_3PO_4 \cdot 3H_2O$ (80 mg, 0.3 mmol) in DMF (2 mL) afforded 67 mg (80 %) of **3af**. Liquid; 1H NMR (300 MHz, CDCl₃) δ 7.46 (d, J = 6.9 Hz, 2 H), 7.22 (d, J = 6.9 Hz, 2 H), 5.46 (dd, J = 10.8, 8.4 Hz, 1 H), 5.41 (s, 1 H), 5.36 (s, 1 H), 4.13 (qd, J = 7.2, 1.2 Hz, 2 H), 3.09 (ddq, J = 14.4, 10.8, 1.5 Hz, 1 H), 2.64 (ddq, J = 14.4, 8.4, 1.5 Hz, 1 H), 2.26 (t, J = 1.5 Hz, 3 H), 1.24 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl₃, 75.4 MHz) δ 167.4, 165.9, 146.2, 137.0, 131.6, 128.3, 122.0, 113.3, 101.8, 82.0, 59.5, 35.8, 14.4, 14.0; MS (EI) m/z (%) 338($M(^{81}Br)^+$, 1.07) 336 ($M(^{79}Br)^+$, 0.91), 43 (100); IR (neat) 2979, 2929, 1698, 1652, 1489, 1384, 1226, 1084; HRMS (EI) calcd for $C_{16}H_{17}O_3Br$ ($M(^{79}Br)^+$) 336.0361. Found 336.0363.

(7) 2-Methyl-5-(1-(naphth-1-yl)vinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3ag)

The reaction of **1a** (46 mg, 0.25 mmol), 1-iodo-naphthalene (77 mg, 0.30 mmol), Pd(PPh₃)₄ (15 mg, 0.013 mmol), and K₃PO₄·3H₂O (81 mg, 0.30 mmol) in DMF (2 mL) afforded 60 mg (77 %) of **3ag**. Liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.07-8.03 (m, 1 H), 7.89-7.81 (m, 2 H), 7.53-7.42 (m, 3 H), 7.37-7.34 (m, 1 H), 5.71 (s, 1 H), 5.47 (t, *J* = 9.6 Hz, 1 H), 5.28 (s, 1 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 2.95-2.86 (m, 1 H), 2.79-2.71 (m, 1 H), 2.27 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 167.5, 166.0, 146.4, 136.6, 133.6, 131.7, 128.2, 128.0, 126.1, 125.8, 125.4, 125.1, 115.9, 101.6, 83.6, 59.4, 35.0, 14.3, 14.0; MS (EI) *m/z* (%) 308 (M⁺, 9.85), 43 (100); IR (neat) 3058, 2979, 2930, 2870, 1698, 1652, 1382, 1323, 1259, 1224, 1137, 1084; HRMS (MALDI/DHB) calcd for C₂₀H₂₀O₃Na (M+Na⁺) 331.1305. Found 331.1312.

(8) 2-Methyl-5-(octa-1,3(*E*)-dien-2-yl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3ah**)**

The reaction of **1a** (45 mg, 0.25 mmol), (*E*)-1-iodohexene (65 mg, 0.31 mmol), Pd(PPh₃)₄ (15 mg, 0.014 mmol), and K₃PO₄·3H₂O (82 mg, 0.3 mmol) in DMF (2 mL) afforded 53 mg (81 %) of **3ah**. Liquid; ¹H NMR (300 MHz, CDCl₃) δ 6.03 (d, *J* = 16.2 Hz, 1 H), 5.61 (dt, *J* = 29.7, 6.6 Hz, 1 H), 5.23 (dd, *J* = 10.8, 8.1 Hz, 1 H), 5.06 (s, 1 H),

5.00 (s, 1 H), 4.15 (q, $J = 7.2$ Hz, 2 H), 3.15 (ddq, $J = 14.4, 10.8, 1.5$ Hz, 1 H), 2.67 (ddq, $J = 14.4, 8.1, 1.5$ Hz, 1 H), 2.24 (t, $J = 1.5$ Hz, 3 H), 2.10 (q, $J = 9.0$ Hz, 2 H), 1.45-1.20 (m, 4 H), 1.26 (t, $J = 6.9$ Hz, 3 H), 0.89 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 167.6, 166.1, 145.2, 131.9, 128.3, 111.5, 101.8, 80.9, 59.4, 36.4, 32.8, 31.3, 22.2, 14.4, 14.0, 13.9; MS (EI) m/z (%) 265 ($\text{M}+\text{H}^+$, 4.06), 264 (M^+ , 0.87), 43 (100); IR (neat) 2957, 2928, 2872, 1702, 1655, 1383, 1326, 1257, 1226, 1084; HRMS (MALDI/DHB) calcd for $\text{C}_{16}\text{H}_{25}\text{O}_3$ ($\text{M}+\text{H}^+$) 265.1798. Found 265.1807.

(9) 2-Methyl-5-(1-(thiophen-2-yl)vinyl)-3-(ethoxycarbonyl)-4,5-dihydrofuran (3ai)

The reaction of **1a** (45 mg, 0.25 mmol), 2-iodo-thiophene (65 mg, 0.31 mmol), $\text{Pd}(\text{PPh}_3)_4$ (15 mg, 0.014 mmol), and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (82 mg, 0.3 mmol) in DMF (2 mL) afforded 55 mg (84 %) of **3ai**. Liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.24-7.21 (m, 1 H), 7.05-6.98 (m, 2 H), 5.51 (s, 1 H), 5.47-5.39 (m, 1 H), 5.24 (s, 1 H), 4.15 (q, $J = 7.2$ Hz, 2 H), 3.21 (ddq, $J = 14.4, 10.8, 1.5$ Hz, 1 H), 2.80 (ddq, $J = 14.4, 8.4, 1.8$ Hz, 1 H), 2.28 (t, $J = 1.5$ Hz, 3 H), 1.25 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 167.4, 165.9, 140.8, 127.4, 124.9, 124.1, 111.0, 102.0, 82.1, 59.5, 36.3, 14.4, 14.0; MS (EI) m/z (%) 264 (M^+ , 0.64), 43 (100); IR (neat) 3105, 2979, 2929, 2870, 1697, 1655, 1438, 1384, 1260, 1225, 1084; HRMS (MALDI/DHB) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{SNa}$ ($\text{M}+\text{Na}^+$) 287.0712. Found 287.0719.

(10) 2-Propyl-5-(1-phenylvinyl)-3-(methoxycarbonyl)-4,5-dihydrofuran (3ba)

The reaction of **1b** (53 mg, 0.25 mmol), PhI (61 mg, 0.30 mmol), $\text{Pd(PPh}_3)_4$ (15 mg, 0.014 mmol), and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (80 mg, 0.3 mmol) in DMF (2 mL) afforded 65 mg (91 %) of **3ba**. Liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.26 (m, 5 H), 5.55-5.48 (m, 1 H), 5.42 (s, 1 H), 5.34 (t, $J = 1.2$ Hz, 1 H), 3.66 (s, 3 H), 3.12 (ddq, $J = 14.4, 11.4, 0.9$ Hz, 1 H), 2.75-2.64 (m, 3 H), 1.70-1.60 (m, 2 H), 0.99 (t, $J = 0.9$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 171.3, 166.3, 147.4, 138.1, 128.4, 127.9, 126.6, 112.3, 101.1, 82.1, 50.7, 36.0, 29.5, 20.2, 13.8; MS (EI) m/z (%) 272 (M^+ , 0.47), 43 (100); IR (neat) 2961, 2873, 1706, 1646, 1435, 1240, 1189, 1102; HRMS (MALDI/DHB) calcd for $\text{C}_{17}\text{H}_{21}\text{O}_3$ ($\text{M}+\text{H}^+$) 273.1485. Found 273.1487.

(11) 2-(i-Propyl)-5-(1-phenylvinyl)-3-(methoxycarbonyl)-4,5-dihydrofuran (3ca)

The reaction of **1c** (52 mg, 0.25 mmol), PhI (61 mg, 0.30 mmol), $\text{Pd(PPh}_3)_4$ (14 mg, 0.014 mmol), and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (80 mg, 0.3 mmol) in DMF (2 mL) afforded 67 mg (93 %) of **3ca**. Liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.26 (m, 5 H), 5.55-5.47 (m, 1 H),

5.40 (s, 1 H), 5.34 (s, 1 H), 3.80-3.60 (m, 1 H), 3.66 (s, 3 H), 3.11 (dd, $J = 14.4, 11.1$ Hz, 1 H), 2.65 (dd, $J = 14.4, 8.4$ Hz, 1 H), 1.21 (d, $J = 6.9$ Hz, 3 H), 1.19 (d, $J = 6.9$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 175.5, 166.2, 147.6, 138.2, 128.4, 127.9, 126.7, 112.1, 99.1, 82.0, 50.7, 36.1, 26.8, 19.64, 19.60; MS (EI) m/z (%) 273 ($\text{M}+\text{H}^+$, 2.09), 272 ($\text{M}+\text{H}^+$, 0.59), 43 (100); IR (neat) 2970, 2873, 1700, 1642, 1469, 1435, 1350, 1265, 1234, 1121, 1066, 1052; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$ (M^+) 272.1412. Found 272.1410.

(12) 2-(1-phenylvinyl)-2,3,5,6,7-pentahydrobenzofuran-4-one (3da)

The reaction of **1d** (24 mg, 0.15 mmol), PhI (37 mg, 0.18 mmol), $\text{Pd}(\text{PPh}_3)_4$ (9 mg, 0.008 mmol), and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (49 mg, 0.18 mmol) in DMF (2 mL) afforded 21 mg (58 %) of **3da**. Liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.26 (m, 5 H), 5.70-5.64 (m, 1 H), 5.42 (s, 1 H), 5.34 (s, 1 H), 3.10-3.01 (m, 1 H), 2.68-2.60 (m, 1 H), 2.52-2.479 (m, 2 H), 2.37-2.32 (m, 2 H), 2.10-2.00 (m, 2 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 195.5, 177.0, 147.0, 138.0, 128.5, 128.1, 126.7, 113.1, 113.0, 85.6, 36.4, 32.2, 23.9, 21.7; MS (EI) m/z (%) 240 (M^+ , 16.55), 184 (100); IR (neat) 2945, 1635, 1402, 1230, 1181; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$ (M^+) 240.1150. Found 240.1154.

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