Supporting Information

Preparation of Ethyl 2-Aryl 2,3-Alkadienoates via Palladium-Catalyzed Selective Cross-Coupling Reactions

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Table of Contents

Experimental procedure and data of compounds -------------------------------- S2-S12
Reference --------------------------------------------------------------------------------- S12
\textsuperscript{1}H and \textsuperscript{13}C NMR spectra for compounds--------------------------------- S13-S52
Experimental Section

General: Reactions were carried out in oven-dried glassware under nitrogen atmosphere. All commercial reagents were used without purification, and all solvents were reaction grade. THF was freshly distilled from Na and benzophenone. DMF was freshly distilled from CaH₂ and dried with molecular sieves (4 Å). All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel 60 F₂₅₄ precoated glass plates, which were visualized with UV light and then developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel 60 (0.040-0.063 mm, 230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded on 400 MHz NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ¹H and δ 77.0 for ¹³C). Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. Mass spectra were recorded on high-resolution mass spectrometer.
General procedure for the preparation of ethyl 4-bromo-2-pentynoate (2b): To a stirred solution of ethyl 4-hydroxy-2-pentynoate$^1$ (71.08 mg, 0.5 mmol) in CH$_2$Cl$_2$ (2 mL) was added Et$_3$N (75.9 mg, 0.75 mmol) and methanesulfonyl chloride (85.88 mg, 0.75 mmol) at 0 °C. After the mixture was stirred for 1 h at that temperature, the reaction was quenched with aqueous H$_2$O, and the mixture was diluted with CH$_2$Cl$_2$ followed by the separation of the resulting organic layer. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 20 mL), and the combined CH$_2$Cl$_2$ layers were washed with sat-NaCl, dried over MgSO$_4$, and evaporated. The residue was added to a solution of lithium bromide (173 mg, 2 mmol) in dry THF (2 mL) with stirring under a nitrogen atmosphere 0 °C. After the mixture was stirred for 5 h at room temperature, the reaction mixture was quenched with saturated H$_2$O. The aqueous layer was extracted with diethyl ether (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1/30 ) give ethyl 4-bromo-2-pentynoate (80.0 mg, 78%). $^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 5.00 (q, $J = 6.9$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.94 (d, $J = 6.9$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, Acetone-$d_6$) $\delta$ 153.8, 86.7, 77.7, 63.3, 29.7, 26.9, 14.6; IR (film) 2984, 2360, 2341, 2253, 1710, 1259 cm$^{-1}$; HRMS (EI) calcd for C$_7$H$_8$BrO$_2$ 203.9786, found 203.9790.
Ethyl 4-bromo-2-heptynoate (2c): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.53 (t, $J = 6.9$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 4.06 (q, $J = 7.2$ Hz, 2H), 1.59 (qint, $J = 7.4$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.5, 85.1, 77.8, 62.7, 40.9, 33.9, 20.9, 14.4, 13.5; IR (film) 2968, 2360, 2341, 2253, 1709, 1257 cm$^{-1}$; HRMS (El) calcd for C$_9$H$_{13}$BrO$_2$ 232.0099, found 232.0097.

General procedure for the preparation of ethyl 2-(4-ethoxycarbonylphenyl)-2,3-butadienoate (3a): To a suspension of Pd$_2$dba$_3$CHCl$_3$ (6.2 mg, 0.6 x 10$^{-2}$ mmol) and (p-$CF_3$-C$_6$H$_4$)$_3$P (22.0 mg, 4.8 x 10$^{-2}$ mmol) in THF (0.5 mL) was added ethyl 4-iodobezolate (1a) (50.5 $\mu$L, 0.3 mmol) at room temperature under nitrogen atmosphere. After being stirred for 30 min, organoindium reagent generated in situ from indium (52.0 mg, 0.45 mmol), sodium iodide (67.5 mg, 0.45 mmol) and ethyl 4-bromo-2-butynoate (129.0 mg, 0.68 mmol) in THF (1.0 mL) was added and the mixture was stirred at 70 $^\circ$C for 2 h. The reaction mixture was quenched with saturated NaHCO$_3$. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 20 mL) and the combined organic layers were washed with brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:hexane = 1:30) to give 3a (62.0 mg, 0.24 mmol, 79%).

![Ethyl 2(4-ethoxycarbonylphenyl)-2,3-butadienoate (3a)](image)

Ethyl 2(4-ethoxycarbonylphenyl)-2,3-butadienoate (3a): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 8.44$ Hz, 2H), 7.60 (d, $J = 8.44$ Hz, 2H), 5.48 (s, 2H), 4.38 (q, $J = 7.09$ Hz, 2H), 4.30 (q, $J = 7.12$ Hz, 2H), 1.39 (t, $J = 7.09$ Hz, 3H), 1.33 (t, $J = 7.12$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 216.2, 166.7, 165.9, 137.1, 129.90, 129.86,
Ethyl 2-phenyl-2,3-butadienoate (3b): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 7.46$ Hz, 2H), 7.35 (t, $J = 7.51$ Hz, 2H), 7.29-7.25 (m, 1H), 5.40 (s, 2H), 4.29 (q, $J = 7.12$ Hz, 2H), 1.33 (t, $J = 7.12$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 215.9, 166.4, 132.5, 128.9, 128.7, 128.1, 103.5, 80.5, 61.8, 14.7; IR (film) 2982, 1956, 1714, 1393, 1250, 1049, 854 cm$^{-1}$; HRMS (EI) calcd for C$_{12}$H$_{12}$O$_2$ M$^+$ 188.0837, found 188.0837.

Ethyl 2-(1-naphthyl)-2,3-butadienoate (3c): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89-7.83 (m, 3H), 7.50-7.46 (m, 5H), 5.32 (s, 2H), 2.32 (s, 3H), 4.26 (q, $J = 7.10$ Hz, 2H), 1.27 (td, $J = 7.10$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 215.4, 166.8, 134.1, 132.2, 130.8, 129.1, 128.9, 128.2, 126.6, 126.2, 125.7, 125.5, 101.7, 79.0, 61.9, 14.7; IR (film) 2983, 1960, 1714, 1393, 1250, 1150, 1091, 851, 777 cm$^{-1}$; HRMS (EI) calcd for C$_{16}$H$_{14}$O$_2$ M$^+$ 238.0994, found 238.0996.
CO₂Et

**Ethyl 2-(4-**\(\text{n}\)-**butylphenyl)**-2,3-**butadienoate (3d):** \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.42 (d, \(J = 8.19\) Hz, 2H), 7.17 (d, \(J = 8.19\) Hz, 2H), 5.39 (s, 2H), 4.30 (q, \(J = 7.16\) Hz, 2H), 2.61 (t, \(J = 7.74\) Hz, 2H), 1.64-1.56 (m, 2H), 1.41-1.32 (m, 2H), 1.34 (t, \(J = 7.16\) Hz, 3H), 0.93 (t, \(J = 7.32\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\) 214.3, 165.1, 141.5, 128.1, 127.4, 127.2, 102.0, 78.9, 60.2, 34.3, 32.5, 21.3, 13.2, 12.9; IR (film) 2930, 1928, 1718, 1511, 1464, 1144, 1037, 840 cm\(^{-1}\); HRMS (EI) calcd for C\(_{16}\)H\(_{20}\)O\(_2\) M\(^+\) 244.1463, found 244.1463.

CO₂Et

**Ethyl 2-(3-methoxyphenyl)**-2,3-**butadienoate (3e):** \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.26 (t, \(J = 7.77\) Hz, 1H), 7.10 (d, \(J = 7.77\) Hz, 2H), 6.85-6.82 (m, 1H), 5.41 (s, 2H), 4.29 (q, \(J = 7.17\) Hz, 2H), 3.81 (s, 3H), 1.33 (t, \(J = 7.17\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\) 215.8, 166.3, 159.9, 133.8, 129.6, 121.3, 114.4, 113.8, 103.4, 80.5, 61.7, 55.7, 14.7; IR (film) 2981, 2835, 1954, 1715, 1598, 1581, 1487, 1453, 1294, 1250, 1035 cm\(^{-1}\); HRMS (EI) calcd for C\(_{13}\)H\(_{14}\)O\(_3\) M\(^+\) 218.0943, found 218.0941.
Ethyl 2-(3-nitrophenyl)-2,3-butadienoate (3f): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.41 (s, 1H), 8.14 (d, $J = 8.00$ Hz, 1H), 7.89 (d, $J = 8.00$ Hz, 1H), 7.52 (t, $J = 8.00$ Hz, 2H), 5.56 (s, 2H), 4.32 (q, $J = 7.14$ Hz, 2H), 1.35 (t, $J = 7.14$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 216.2, 165.6, 148.6, 134.8, 134.5, 129.5, 123.8, 122.8, 102.0, 81.9, 62.1, 14.6; IR (film) 2984, 1953, 1715, 1347, 1248, 1153, 1039 cm$^{-1}$; HRMS (EI) calcd for C$_{12}$H$_{11}$NO$_4$ M$^+$ 233.0688, found 233.0685.

![Ethyl 2-(3-nitrophenyl)-2,3-butadienoate (3f)](image-url)

Ethyl 2-(4-acetylphenyl)-2,3-butadienoate (3g): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J = 8.44$ Hz, 2H), 7.63 (d, $J = 8.44$ Hz, 2H), 5.49 (s, 2H), 4.31 (q, $J = 7.12$ Hz, 2H), 2.60 (s, 3H), 1.34 (t, $J = 7.12$ Hz, 3H), 0.93 (t, $J = 7.34$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 216.3, 198.1, 165.9, 137.4, 136.4, 128.9, 128.7, 102.9, 81.2, 61.9, 27.0, 14.6; IR (film) 2981, 1952, 1716, 1683, 1603, 1268, 1147, 844 cm$^{-1}$; HRMS (EI) calcd for C$_{14}$H$_{14}$O$_3$ M$^+$ 230.0943, found 230.0941.

![Ethyl 2-(4-acetylphenyl)-2,3-butadienoate (3g)](image-url)

Ethyl 2-(2-methylphenyl)-2,3-pentadienoate (3h): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.22-7.18 (m, 4H), 5.62 (q, $J = 7.38$ Hz, 1H), 4.24 (q, $J = 7.12$ Hz, 2H), 2.28 (s, 3H), 1.83 (d, $J = 7.38$ Hz, 3H), 1.28 (t, $J = 7.12$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 211.8, 167.0, 137.0, 133.7, 130.6, 128.3, 126.1, 102.1, 89.7, 61.6, 20.5, 14.7, 13.4; IR
(film) 2979, 1954, 1714, 1458, 1267, 1228, 1144, 1033, 744 cm\(^{-1}\); HRMS (EI) calcd for C\(_{14}\)H\(_{18}\)O\(_2\) M\(^+\) 216.1150, found 216.1148.

![Ethyl 2-(4-formylphenyl)-2,3-pentadienoate (3i):](image)

**Ethyl 2-(4-formylphenyl)-2,3-pentadienoate (3i):** \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.01 (s, 1H), 7.85 (d, \(J = 8.34\) Hz, 2H), 7.68 (d, \(J = 8.34\) Hz, 2H), 5.88 (q, \(J = 7.35\) Hz, 1H), 4.30 (q, \(J = 7.09\) Hz, 2H), 1.91 (d, \(J = 7.35\) Hz, 3H), 1.33 (t, \(J = 7.09\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 213.3, 192.3, 166.2, 140.0, 135.6, 130.0, 129.3, 102.6, 92.2, 61.8, 14.7, 13.4; IR (film) 2981, 1944, 1717, 1604, 1368, 1280, 1213, 1172, 1036, 835 cm\(^{-1}\); HRMS (EI) calcd for C\(_{14}\)H\(_{14}\)O\(_3\) M\(^+\) 230.0943, found 230.0938.

![Ethyl 2-(2-ethoxycarbonylphenyl)-2,3-pentadienoate (3j):](image)

**Ethyl 2-(2-ethoxycarbonylphenyl)-2,3-pentadienoate (3j):** \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 7.62\) Hz, 1H), 7.48 (t, \(J = 7.52\) Hz, 1H), 7.37 (t, \(J = 7.43\) Hz, 1H), 7.30 (d, \(J = 7.55\) Hz, 1H), 5.74 (q, \(J = 7.32\) Hz, 1H), 4.29 (q, \(J = 7.13\) Hz, 2H), 4.20 (q, \(J = 7.15\) Hz, 2H), 1.96 (d, \(J = 7.32\) Hz, 3H), 1.35 (t, \(J = 7.13\) Hz, 3H), 1.25 (t, \(J = 7.15\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 211.0, 167.6, 166.8, 135.5, 132.3, 131.9, 130.70, 130.66, 128.2, 104.5, 91.0, 61.5, 61.4, 14.6, 14.5, 13.7; IR (film) 2981, 1944, 1704, 1604, 1368, 1280, 1213, 1172, 1036, 835 cm\(^{-1}\); HRMS (EI) calcd for C\(_{16}\)H\(_{16}\)O\(_4\) M\(^+\) 274.1205, found 274.1207.
Ethyl 2-(4-ethoxycarbonylphenyl)-2,3-pentadienoate (3k): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J$ = 8.46 Hz, 2H), 7.58 (d, $J$ = 8.46 Hz, 2H), 5.84 (q, $J$ = 7.39 Hz, 1H), 4.29 (q, $J$ = 7.13 Hz, 2H), 1.89 (d, $J$ = 7.39 Hz, 3H), 1.39 (t, $J$ = 7.16 Hz, 3H), 1.32 (t, $J$ = 7.13 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 213.0, 166.8, 166.4, 138.3, 129.8, 129.7, 128.7, 102.7, 91.9, 61.7, 61.3, 14.7, 14.6, 13.4; IR (film) 2980, 1944, 1717, 1607, 1446, 1367, 1275, 1146, 1106, 780 cm$^{-1}$; HRMS (EI) calcd for C$_{16}$H$_{18}$O$_4$ M$^+$ 274.1205, found 274.1205.

Ethyl 2-(4-N-benzylcarbonylphenyl)-2,3-pentadienoate (3l): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J$ = 8.40 Hz, 2H), 7.55 (d, $J$ = 8.40 Hz, 2H), 7.36-7.27 (m, 5H), 6.54 (bs, 1H), 5.83 (q, $J$ = 7.39 Hz, 1H), 4.63 (d, $J$ = 5.70 Hz, 2H), 4.27 (q, $J$ = 7.09 Hz, 2H), 1.88 (d, $J$ = 7.39 Hz, 3H), 1.32 (t, $J$ = 7.09 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 212.9, 167.4, 166.5, 138.6, 137.0, 133.5, 129.2, 129.0, 128.3, 128.0, 127.3, 102.6, 91.9, 61.7, 44.5, 14.7, 13.4; IR (film) 3320, 2979, 1944, 1714, 1639, 1501, 1280, 1223, 857 cm$^{-1}$; HRMS (EI) calcd for C$_{21}$H$_{21}$NO$_3$ M$^+$ 335.1521, found 335.1521.
Ethyl 2-phenyl-2,3-heptadienoate (3m): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 2.95$ Hz, 2H), 7.33 (t, $J = 6.79$ Hz, 2H), 7.28-7.23 (m, 1H), 5.79 (t, $J = 5.79$ Hz, 1H), 4.30-4.24 (m, 2H), 2.21 (q, $J = 7.18$ Hz, 2H), 1.59-1.52 (m, 2H), 1.31 (t, $J = 17.62$ Hz, 3H), 0.98 (t, $J = 7.41$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 212.0, 166.9, 133.6, 128.8, 128.6, 127.8, 103.6, 96.3, 61.5, 30.5, 22.6, 14.7, 14.0; IR (film) 2960, 1946, 1716, 1448, 1209, 1145, 1026 cm$^{-1}$; HRMS (EI) calcd for C$_{15}$H$_{18}$O$_2$ M$^+$ 230.1307, found 230.1304.

![Ethyl 2-phenyl-2,3-heptadienoate](image)

Ethyl 2-(3-methoxyphenyl)-2,3-heptadienoate (3n): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27-7.23 (m, 1H), 7.11-7.08 (m, 2H), 6.83-6.80 (m, 1H), 5.79 (t, $J = 7.05$ Hz, 1H), 4.30-4.24 (m, 2H), 3.80 (s, 3H), 2.20 (q, $J = 7.11$ Hz, 2H), 1.58-1.52 (m, 2H), 1.31 (t, $J = 7.57$ Hz, 3H), 0.98 (t, $J = 7.38$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 211.9, 166.8, 159.8, 134.9, 129.5, 121.3, 114.4, 113.4, 103.4, 96.4, 61.5, 55.6, 30.5, 22.6, 14.7, 14.0; IR (film) 2959, 1943, 1715, 1598, 1463, 1240, 1036 cm$^{-1}$; HRMS (EI) calcd for C$_{16}$H$_{20}$O$_3$ M$^+$ 260.1412, found 260.1412.

![Ethyl 2-(3-methoxyphenyl)-2,3-heptadienoate](image)

Ethyl 2-(4-ethoxycarbonylphenyl)-2,3-heptadienoate (3o): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 8.43$ Hz, 2H), 7.60 (d, $J = 8.43$ Hz, 2H), 5.86 (t, $J = 7.06$ Hz, 1H), 4.37 (q, $J = 7.12$ Hz, 2H), 4.31-4.25 (m, 2H), 1.58-1.52 (m, 2H), 1.39 (t, $J = 7.12$ Hz,
1,4-Bis(1-ethoxycarbonyl-1,2-propadien-1-yl)benzene (3p): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (s, 4H), 5.42 (s, 4H), 4.30 (q, $J = 7.14$ Hz, 4H), 1.33 (t, $J = 7.14$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 215.9, 166.3, 131.7, 128.7, 103.2, 61.8, 14.7; IR (film) 3407, 2981, 1926, 1715, 1509, 1243, 1151 cm$^{-1}$; HRMS (EI) calcd for C$_{18}$H$_{18}$O$_4$ M$^+$ 298.1205, found 298.1206.

Ethyl 2-(4-tert-butyl-1-cyclohexen-1-yl)-2,3-butadienoate (3q): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.15-6.14 (m, 1H), 5.24 (s, 2H), 4.26(q, $J = 7.13$ Hz, 2H), 2.23-2.10 (m, 4H), 1.97-1.83 (m, 3H), 1.30 (t, $J = 7.13$ Hz, 3H), 0.87 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 213.8, 166.6, 128.4, 128.3, 105.0, 80.3, 61.4, 44.0, 32.6, 29.3, 27.9, 27.6, 24.4, 14.6; IR (film) 2960, 1723, 1469, 1365, 1238, 1028 cm$^{-1}$; HRMS (EI) calcd for C$_{16}$H$_{24}$O$_2$ M$^+$ 248.1776, found 248.1779.
4-(Ethoxycarbonyl-1,2-propadien-1-yl)-8-methoxy-1,2-dihydronaphthalene (3r):

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 (t, $J = 8.00$ Hz, 1H), 6.76 (t, $J = 8.73$ Hz, 2H) 6.12 (t, $J = 4.60$ Hz, 1H), 5.22 (s, 2H), 4.18 (q, $J = 7.15$ Hz, 2H), 3.82 (s, 3H), 2.83 (t, $J = 8.23$ Hz, 2H), 2.35-2.30 (m, 2H), 1.22 (t, $J = 7.15$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$215.1, 166.8, 156.5, 135.2, 131.5, 130.9, 126.7, 124.3, 117.5, 110.3, 102.2, 78.5, 61.7, 56.0, 23.3, 19.9, 14.6; IR (film) 2981, 2835, 1959, 1716, 1573, 1469, 1342, 1260, 1132, 843 cm$^{-1}$; HRMS (El) calcd for C$_{17}$H$_{18}$O$_3$ M$^+$ 270.1256, found 270.1256.

References
