Supporting Information

Palladium Catalyzed Allylation of α -nitroacetates with propynes

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General Consideration

All solvents and reagents were purchased from the suppliers and used without further purification. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 at room temperature on the Varian INOVA-400 spectrometer (400 MHz ^1H) and Bruker spectrometer (400 MHz ^1H). The chemical-shifts scale is based on internal TMS. All reactions were carried out under dry nitrogen atmosphere.

Typical procedure

To a mixture of 1-phenyl-1-propyne (**1a**, 1.0 mmol), ethyl 2-nitrobutanoate (**2a**, 1.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (116mg, 0.1mmol) in dry dioxane (3 mL) was added acetic acid (14 μL , 0.5mmol), and the mixture was stirred 100 $^\circ\text{C}$ for 15 h under a balloon of nitrogen. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (25 mL) and water (25 mL). The aqueous layer was extracted with dichloromethane (3x25 mL) and washed with brine. The organic layers were combined, dried with MgSO_4 , filtered, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate=50:1) to afford the desired product (E)-ethyl 2-ethyl-2-nitro-5-phenylpent-4-enoate (**3a**) in 77% yield.

Spectral Data for Products

(E)-ethyl 2-ethyl-2-nitro-5-phenylpent-4-enoate (3a)^[1]: Yield: 77%; Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.25 (m, 5H), 6.50 (d, J = 15.6 Hz, 1H), 5.96 (dt, J = 15.6 Hz, 7.4 Hz, 1H), 4.28 (q, J = 6.4 Hz, 2H), 3.15-3.04 (m, 2H), 2.36-2.20 (m, 2H), 1.28 (t, J = 7.0 Hz, 3H), 0.96 (t, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.48, 136.38, 135.70, 128.56, 127.88, 126.34, 120.58, 96.18, 62.66, 37.07, 27.02, 13.90, 7.93; MS (m/z , %): 277 [M^+]; IR/ cm^{-1} : 2939, 1749

(COO), 1608 (C=C), 1554 (NO₂).

(E)-ethyl 2-methyl-2-nitro-5-phenylpent-4-enoate (3b)^[2-3]: Yield: 82%; Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.26 (m, 5H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.02 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.29 (q, *J* = 6.8 Hz, 2H), 3.18-3.13 (m, 1H), 3.05-3.00 (m, 1H), 1.81 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.08, 136.34, 136.19, 128.58, 127.93, 126.37, 120.66, 92.29, 62.87, 40.22, 21.25, 13.85; MS (*m/z*, %): 263 [M⁺]; IR/cm⁻¹: 2939, 1749 (COO), 1608 (C=C), 1554 (NO₂).

(E)-ethyl 2-(3-phenyl)-allyl-2-nitrohexanoate (3c): Yield: 87%; Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.17 (m, 5H), 6.42 (d, *J* = 15.6 Hz, 1H), 5.89 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.19 (q, *J* = 6.8 Hz, 2H), 3.08-2.96 (m, 2H), 2.21-2.08 (m, 2H), 1.32-1.18 (m, 4H), 1.19 (t, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.56, 136.40, 135.67, 128.54, 127.86, 126.32, 120.67, 95.76, 62.63, 37.53, 33.37, 25.48, 22.49, 13.87, 13.70; HRMS (ESI, *m/z*): calcd for C₁₇H₂₃NO₄ [M⁺]: 305.1627; Found: 305.1634; IR/cm⁻¹: 2937, 1749 (COO), 1608 (C=C), 1552 (NO₂).

(E)-ethyl 5-(4-methoxyphenyl)-2-methyl-2-nitropent-4-enoate (3d): Yield: 80%; Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.86 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.31-4.24 (m, 2H), 3.79 (s, 3H), 3.15-3.09 (m, 1H), 3.02-2.96 (m, 1H), 1.79 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.09, 159.36, 135.52, 129.09, 127.51, 118.19, 113.89, 92.35, 62.77, 55.20, 40.18, 21.14, 13.79; HRMS (ESI, *m/z*): calcd for C₁₅H₁₉NO₅ [M⁺]: 293.1263; Found: 293.1260; IR/cm⁻¹: 2939, 1749 (COO), 1608 (C=C), 1554 (NO₂), 1512, 1298 (-O-), 1248, 1176, 1128, 1033, 970, 856.

(E)-ethyl 2-ethyl-5-(4-methoxyphenyl)-2-nitropent-4-enoate (3e): Yield: 87%; Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.81 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.12-3.00 (m, 2H), 2.35-2.18 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.46, 159.34, 135.02, 129.14, 127.46, 118.10, 113.88, 96.23, 62.53, 55.16, 37.03, 26.89, 13.83, 7.85; HRMS (ESI, *m/z*): calcd for C₁₆H₂₁NO₅ [*M*⁺]: 307.1420; Found: 307.1414; IR/cm⁻¹: 2937, 1749 (COO), 1608 (C=C), 1552 (NO₂), 1510, 1294 (-O-), 1248, 1176, 1032, 970, 858.

(E)-ethyl 2-(3-(4-methoxyphenyl)allyl)-2-nitrohexanoate (3f): Yield: 84%; Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.81 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.13-3.00 (m, 2H), 2.28-2.13 (m, 2H), 1.41-1.20 (m, 4H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.61, 159.36, 135.05, 129.20, 127.50, 118.24, 113.91, 95.86, 62.56, 55.21, 37.54, 33.29, 25.45, 22.47, 13.86, 13.68; HRMS (ESI, *m/z*): calcd for C₁₈H₂₅NO₅ [*M*⁺]: 335.1733; Found: 335.1730; IR/cm⁻¹: 2958, 1749 (COO), 1608 (C=C), 1552 (NO₂), 1512, 1296 (-O-), 1248, 1176, 1034, 970, 858.

(E)-ethyl 2-benzyl-5-(4-methoxyphenyl)-2-nitropent-4-enoate (3g): Yield: 90%; Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.27 (m, 5H), 7.15-7.12 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 15.6 Hz, 1H), 5.90 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.28-4.19 (m, 2H), 3.79 (s, 3H), 3.63-3.50 (m, 2H), 2.95 (d, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.17, 159.42, 135.39, 132.98, 129.93, 129.17, 128.67, 127.86, 127.52, 118.21, 113.95, 96.22, 62.75, 55.21, 39.60, 36.96, 13.80; HRMS (ESI, *m/z*): calcd for C₂₁H₂₃NO₅ [*M*⁺]: 369.1576; Found: 369.1569; IR/cm⁻¹: 2933, 1751 (COO), 1606 (C=C), 1554 (NO₂), 1510, 1302 (-O-), 1246, 1176, 1034, 972, 860.

(E)-ethyl 5-(4-ethoxyphenyl)-2-methyl-2-nitropent-4-enoate (3h): Yield: 80%; Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.86 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.30-4.24 (m, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.14-3.09 (m, 1H), 3.02-2.96 (m, 1H), 1.79 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.09, 158.79, 135.60, 129.00, 127.51, 118.12, 114.49, 92.38, 63.40, 62.74, 40.21, 21.15, 14.70, 13.78; HRMS (ESI, *m/z*): calcd for C₁₆H₂₁NO₅ [*M*⁺]: 307.1420; Found: 307.1426; IR/cm⁻¹: 2929, 1749 (COO), 1606 (C=C), 1554 (NO₂), 1510, 1387, 1300 (-O-), 1246, 1176, 1045, 972, 860.

(E)-ethyl 5-(4-ethoxyphenyl)-2-ethyl-2-nitropent-4-enoate (3i): Yield: 92%; Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.80 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.01 (q, *J* = 6.8 Hz, 2H), 3.12-3.00 (m, 2H), 2.35-2.18 (m, 2H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.48, 158.76, 135.11, 129.03, 127.47, 118.01, 114.46, 96.26, 63.38, 62.53, 37.07, 26.92, 14.69, 13.84, 7.86; HRMS (ESI, *m/z*): calcd for C₁₇H₂₃NO₅ [*M*⁺]: 321.1576; Found: 321.1571; IR/cm⁻¹: 2939, 1749 (COO), 1606 (C=C), 1552 (NO₂), 1510, 1298 (-O-), 1244, 1176, 1045, 970, 858.

(E)-ethyl 2-(3-(4-ethoxyphenyl)allyl)-2-nitrohexanoate (3j): Yield: 89%; Yellow oil. ¹H

NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 15.6 Hz, 1H), 5.80 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.01 (q, *J* = 6.8 Hz, 2H), 3.12-3.00 (m, 2H), 2.28-2.13 (m, 2H), 1.41-1.25 (m, 4H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.60, 158.76, 135.11, 129.08, 127.49, 118.13, 114.48, 95.87, 63.40, 62.54, 37.56, 33.30, 25.46, 22.47, 14.71, 13.85, 13.66;

111 HRMS (ESI, m/z): calcd for $C_{19}H_{27}NO_5$ [M^+]: 349.1889; Found: 349.1896; IR/ cm^{-1} : 2930, 1749
112 (COO), 1608 (C=C), 1551 (NO₂), 1510, 1294 (-O-), 1246, 1176, 1045, 968, 858.

113 **(E)-ethyl 2-benzyl-5-(4-ethoxyphenyl)-2-nitropent-4-enoate (3k)**: Yield: 95%; Yellow oil.

114 ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.26 (m, 5H), 7.15-7.12 (m, 2H), 6.84 (d, J = 8.8 Hz, 2H),
115 6.45 (d, J = 15.6 Hz, 1H), 5.89 (dt, J = 15.6 Hz, 7.6 Hz, 1H), 4.27-4.19 (m, 2H), 4.01 (q, J = 7.2
116 Hz, 2H), 3.63-3.50 (m, 2H), 2.95 (d, J = 7.2 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H), 1.23 (t, J = 7.2 Hz,
117 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.17, 158.79, 135.44, 132.98, 129.92, 129.01, 128.65,
118 127.84, 127.50, 118.04, 114.48, 96.21, 63.39, 62.73, 39.57, 36.95, 14.71, 13.79; HRMS (ESI, m/z):
119 calcd for $C_{22}H_{25}NO_5$ [M^+]: 383.1733; Found: 383.1742; IR/ cm^{-1} : 2922, 1751 (COO), 1606 (C=C),
120 1558 (NO₂), 1508, 1292 (-O-), 1174, 1047, 968, 856.

121 **(E)-ethyl 5-(4-acetylphenyl)-2-methyl-2-nitropent-4-enoate (3l)**: Yield: 68%; Yellow oil.

122 ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 15.6
123 Hz, 1H), 6.18 (dt, J = 15.6 Hz, 7.6 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.21-3.15 (m, 1H), 3.08-3.02
124 (m, 1H), 2.59 (s, 3H), 1.83 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 197.40,
125 166.86, 140.78, 136.22, 135.04, 128.67, 126.38, 123.81, 92.07, 62.90, 40.17, 26.49, 21.26, 13.76;
126 HRMS (ESI, m/z): calcd for $C_{16}H_{19}NO_5$ [M^+]: 305.1263; Found: 305.1266; IR/ cm^{-1} : 2926, 1749
127 (COO), 1682 (CO), 1605 (C=C), 1554 (NO₂), 1360, 1182, 1128, 972, 856.

128 **(E)-ethyl 5-(4-acetylphenyl)-2-ethyl-2-nitropent-4-enoate (3m)**: Yield: 70%; Yellow oil.

129 ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 16.0
130 Hz, 1H), 6.13 (dt, J = 16.0 Hz, 7.6 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.18-3.06 (m, 2H), 2.59 (s,
131 3H), 2.37-2.21 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100
132 MHz) δ 197.38, 166.26, 140.81, 136.19, 134.58, 128.66, 126.35, 123.78, 96.00, 62.69, 37.12,

27.15, 26.48, 13.82, 7.90; HRMS (ESI, m/z): calcd for $C_{17}H_{21}NO_5$ [M^+]: 319.1420; Found: 319.1428; IR/ cm^{-1} : 2924, 1749 (COO), 1684 (CO), 1605 (C=C), 1552 (NO₂), 1362, 1240, 1097, 970, 858.

(E)-ethyl 2-(3-(4-acetylphenyl)allyl)-2-nitrohexanoate (3n): Yield: 69%; Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 15.6 Hz, 1H), 6.13 (dt, J = 15.6 Hz, 7.6 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.18-3.06 (m, 2H), 2.58 (s, 3H), 2.30-2.16 (m, 2H), 1.41-1.26 (m, 4H), 1.28 (t, J = 7.0 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 197.35, 166.35, 140.83, 136.19, 134.55, 128.65, 126.35, 123.88, 95.59, 62.68, 37.60, 33.50, 26.46, 25.44, 22.40, 13.81, 13.61; HRMS (ESI, m/z): calcd for $C_{19}H_{25}NO_5$ [M^+]: 347.1733; Found: 347.1728; IR/ cm^{-1} : 2960, 1747 (COO), 1684 (CO), 1603 (C=C), 1554 (NO₂), 1362, 1213, 970, 858.

(E)-ethyl 5-(4-acetylphenyl)-2-benzyl-2-nitropent-4-enoate (3o): Yield: 67%; Light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.35-7.28 (m, 3H), 7.17-7.13 (m, 2H), 6.55 (d, J = 15.6 Hz, 1H), 6.21 (dt, J = 15.6 Hz, 7.6 Hz, 1H), 4.32-4.20 (m, 2H), 3.66-3.53 (m, 2H), 3.00 (d, J = 7.2 Hz, 2H), 2.58 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 197.36, 165.96, 140.81, 136.25, 134.83, 132.70, 129.87, 128.72, 128.69, 127.96, 126.36, 123.90, 95.97, 62.87, 39.90, 37.13, 26.48, 13.77; HRMS (ESI, m/z): calcd for $C_{22}H_{23}NO_5$ [M^+]: 381.1576; Found: 381.1567; IR/ cm^{-1} : 2983, 1753 (COO), 1676 (CO), 1603 (C=C), 1552 (NO₂), 1360, 1271 (-O-), 1192, 974, 706.

(E)-ethyl 2-methyl-2-nitro-5-(4-pentanoylphenyl)pent-4-enoate (3p): Yield: 72%; Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.17 (dt, J = 15.6 Hz, 7.6 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.20-3.15 (m, 1H),

155 3.07-3.02 (m, 1H), 2.94 (t, $J = 7.4$ Hz, 2H), 1.82 (s, 3H), 1.75-1.67 (m, 2H), 1.45-1.36 (m, 2H),
156 1.29 (t, $J = 7.0$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 199.78, 166.84,
157 140.54, 136.17, 135.08, 128.39, 126.36, 123.61, 92.07, 62.86, 40.16, 38.19, 26.40, 22.35, 21.23,
158 13.82, 13.74; HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_5$ [M^+]: 347.1733; Found: 347.1738; IR/cm^{-1} :
159 2962, 1749 (COO), 1684 (CO), 1605 (C=C), 1554 (NO_2), 1209, 1180, 1011, 972, 858.

160 **(E)-ethyl 2-ethyl-2-nitro-5-(4-pentanoylphenyl)pent-4-enoate (3q)**: Yield: 78%; Yellow
161 oil. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.54 (d, $J =$
162 15.6 Hz, 1H), 6.12 (dt, $J = 15.6$ Hz, 7.6 Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 3.17-3.06 (m, 2H), 2.94
163 (t, $J = 7.4$ Hz, 2H), 2.37-2.21 (m, 2H), 1.74-1.67 (m, 2H), 1.45-1.36 (m, 2H), 1.28 (t, $J = 7.0$ Hz,
164 3H), 0.97 (t, $J = 7.6$ Hz, 3H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 199.76,
165 166.24, 140.57, 136.14, 134.62, 128.38, 126.32, 123.58, 95.99, 62.65, 38.18, 37.11, 27.13, 26.40,
166 22.34, 13.82, 13.81, 7.87; HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_5$ [M^+]: 361.1889; Found:
167 361.1882; IR/cm^{-1} : 2962, 1749 (COO), 1684 (CO), 1603 (C=C), 1552 (NO_2), 1209, 1182, 1024,
168 970, 858.

169 **(E)-ethyl 2-nitro-2-(3-(4-pentanoylphenyl)allyl)hexanoate (3r)**: Yield: 76%; Yellow oil.
170 ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.53 (d, $J = 15.6$
171 Hz, 1H), 6.12 (dt, $J = 16.0$ Hz, 7.6 Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 3.17-3.05 (m, 2H), 2.94 (t, J
172 = 7.4 Hz, 2H), 2.30-2.16 (m, 2H), 1.75-1.67 (m, 2H), 1.45-1.34 (m, 4H), 1.32-1.19 (m, 2H), 1.28
173 (t, $J = 7.2$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz)
174 δ 199.76, 166.36, 140.60, 136.15, 134.61, 128.39, 126.33, 123.68, 95.60, 62.66, 38.19, 37.60,
175 33.49, 26.41, 25.44, 22.41, 22.36, 13.83, 13.81, 13.61; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_5$
176 [M^+]: 389.2202; Found: 389.2205; IR/cm^{-1} : 2956, 1749 (COO), 1684 (CO), 1603 (C=C), 1554

(NO₂), 1211, 1180, 970, 856.

(E)-ethyl 2-benzyl-2-nitro-5-(4-pentanoylphenyl)pent-4-enoate (3s): Yield: 71%; Yellow

oil. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.34-7.28 (m, 3H), 7.15-7.13 (m, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 15.6 Hz, 7.6 Hz, 1H), 4.31-4.20 (m, 2H), 3.65-3.53 (m, 2H), 2.99 (d, *J* = 7.2 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.75-1.68 (m, 2H), 1.45-1.36 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 199.80, 165.98, 140.60, 136.23, 134.91, 132.73, 129.89, 128.73, 128.45, 127.96, 126.36, 123.72, 95.99, 62.87, 39.91, 38.23, 37.14, 26.44, 22.39, 13.86, 13.78; HRMS (ESI, *m/z*): calcd for C₂₅H₂₉NO₅ [M⁺]: 423.2046; Found: 423.2050; IR/ cm⁻¹: 2953, 1748 (COO), 1684 (CO), 1605 (C=C), 1554 (NO₂), 1097, 968, 856.

(E)-ethyl 3-methoxy-2-methyl-2-nitro-5-phenylpent-4-enoate (3t): Yield: 39%; Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.41-7.29 (m, 5H), 6.77-6.70 (m, 1H), 6.14-6.02 (m, 1H), 4.76 (d, *J* = 7.2 Hz, 0.60H), 4.62 (d, *J* = 7.6 Hz, 0.33H), 4.32-4.20 (m, 2H), 3.38 (s, 1.11H), 3.36 (s, 1.79H), 1.80 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 1.23H), 1.24 (t, *J* = 7.2 Hz, 2.12H); ¹³C NMR (CDCl₃, 100 MHz) δ 165.46, 165.29, 137.22, 137.14, 137.10, 136.37, 135.63, 128.68, 128.65, 128.49, 128.33, 127.80, 127.78, 127.76, 126.84, 126.77, 122.51, 122.14, 95.03, 94.41, 80.65, 80.61, 71.55, 71.33, 62.87, 62.83, 17.73, 16.05, 13.75; HRMS (ESI, *m/z*): calcd for C₁₅H₁₉NO₅ [M⁺]: 293.1263; Found: 293.1260; IR/cm⁻¹: 2953, 1748 (COO), 1605 (C=C), 1552 (NO₂), 1120 (-O-).

(E)-ethyl 2-ethyl-3-methoxy-2-nitro-5-phenylpent-4-enoate (3u): Yield: 35%; Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.44-7.27 (m, 5H), 6.73 (d, *J* = 6.0 Hz, 0.45H), 6.69 (d, *J* = 5.6 Hz, 0.50H), 6.20-6.11 (m, 1H), 4.54 (d, *J* = 7.6 Hz, 0.48H), 4.48 (d, *J* = 8.4 Hz, 0.54H), 4.33-4.26 (m, 2H), 3.36 (s, 3H), 2.43-2.19 (m, 2H), 1.32-1.27 (m, 3H), 1.01 (t, *J* = 7.6 Hz, 1.43H), 0.96 (t, *J* =

199 7.4 Hz, 1.62H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.28, 165.26, 136.31, 136.02, 135.76, 135.74,
200 128.69, 128.68, 128.42, 126.84, 126.79, 122.55, 122.42, 98.62, 98.34, 83.14, 82.62, 62.57, 62.53,
201 57.72, 57.35, 27.20, 25.87, 13.96, 13.91, 8.79, 8.33; HRMS (ESI, m/z): calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_5$ [M^+]:
202 307.1420; Found: 307.1413; IR/ cm^{-1} : 2953, 1748 (COO), 1605 (C=C), 1552 (NO_2), 1120 (-O-).

203 **(E)-ethyl 3-(benzyloxy)-2-methyl-2-nitro-5-phenylpent-4-enoate (3v):** Yield: 27%;
204 Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.27 (m, 10H), 6.79-6.72 (m, 1H), 6.22-6.09 (m,
205 1H), 5.03 (d, J = 6.8 Hz, 0.50H), 4.86 (d, J = 6.8 Hz, 0.50H), 4.69-4.62 (m, 1H), 4.50-4.45 (m,
206 1H), 4.29-4.15 (m, 2H), 1.85 (s, 3H), 1.22 (t, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ
207 165.33, 136.84, 136.15, 135.65, 128.68, 128.64, 128.46, 126.82, 126.75, 122.21, 121.84, 95.00,
208 94.29, 82.91, 82.62, 62.88, 62.82, 57.56, 57.54, 17.55, 15.96, 13.84, 13.75; HRMS (ESI, m/z):
209 calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_5$ [M^+]: 369.1576; Found: 369.1580; IR/ cm^{-1} : 2953, 1749 (COO), 1605 (C=C),
210 1550 (NO_2), 1130 (-O-).

211 **(E)-ethyl 3-(benzyloxy)-2-ethyl-2-nitro-5-phenylpent-4-enoate (3w):** Yield: 25%; Yellow
212 oil. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.28 (m, 10H), 6.74 (d, J = 6.8 Hz, 0.46H), 6.70 (d, J =
213 6.8 Hz, 0.53H), 6.29-6.20 (m, 1H), 4.81 (d, J = 7.6 Hz, 0.49H), 4.71 (d, J = 8.0 Hz, 0.53H),
214 4.68-4.65 (m, 1H), 4.49-4.45 (m, 1H), 4.29-4.22 (m, 2H), 2.41-2.24 (m, 2H), 1.28-1.21 (m, 3H),
215 0.99 (t, J = 6.6 Hz, 1.55H), 0.91 (t, J = 6.8 Hz, 1.56H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.33,
216 165.19, 137.29, 137.19, 136.58, 136.24, 135.72, 128.67, 128.45, 128.30, 128.27, 127.74, 127.69,
217 126.86, 126.79, 122.82, 98.67, 98.31, 80.94, 80.25, 71.48, 70.93, 62.55, 62.50, 27.13, 25.77, 13.86,
218 8.81, 8.26; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_5$ [M^+]: 383.1733; Found: 383.1739; IR/ cm^{-1} :
219 2953, 1749 (COO), 1605 (C=C), 1550 (NO_2), 1130 (-O-).

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References

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243 Copies of ^1H , ^{13}C NMR spectra

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