General and Selective Synthesis of (Z)-3-Haloacrylates via Palladium-Catalyzed Carbonylation of Terminal Alkynes

Jin-Heng Li,* Shi Tang, and Ye-Xiang Xie

Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

jhli@hunnu.edu.cn

Supporting Information

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(A) General

All reagents were directly used as obtained commercially.

(B) Typical experimental procedure

Typical experimental procedure for the palladium-catalyzed carbonylation of terminal alkynes. A mixture of alkyne **1** (1.0 mmol), PdX₂ (5 mol%), CuX₂ (5 equiv), DCE (10 mL) and MeOH (the amount indicated in Table 1) was stirred under an atmospheric pressure of CO at room temperature for 5 h until complete consumption of starting material as judged by TLC and GC analysis. Then the mixture was filtered and evaporated, the residue was purified by flash column chromatography to afford **3–19** (hexane/ethyl acetate).

(C) Analytical data for 3–19

(Z)-Methyl 3-bromooct-2-enoate (3): Colorless oil; ¹H NMR (400 MHz) δ: 6.29 (s, 1H), 3.75 (s, 3H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.61 (m, 2H), 1.34 – 1.31 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz) δ: 164.7, 142.7, 118.9, 51.5, 43.6, 30.6, 27.0, 22.3, 13.9; IR (CH₂Cl₂): 1731, 1633 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 236 (M⁺ + 2, 3), 234 (M⁺, 4), 205 (18), 203 (22), 155 (M⁺ - Br, 100); HRMS (EI) for C₉H₁₅⁷⁹BrO₂ (M⁺): calcd. 234.0255, found 234.0254.

(Z)-Methyl 3-bromoundec-2-enoate (4): Colorless oil; ¹H NMR (400 MHz) δ: 6.29 (s, 1H), 3.75 (s, 3H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.64 – 1.60 (m, 2H), 1.30 – 1.27 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz) δ: 164.7, 142.9, 118.8, 51.5, 43.5, 31.8, 29.2, 29.1, 28.4, 27.9, 22.6, 14.1; IR (CH₂Cl₂): 1730, 1636 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 278 (M⁺ + 2, 2), 276 (M⁺, 3), 247 (16), 245 (19), 197 (M⁺ - Br, 100); HRMS (EI) for C₁₂H₂₁⁷⁹BrO₂ (M⁺): calcd. 276.0725, found 276.0725.

(Z)-Butyl 3-bromoundec-2-enoate (5): Colorless oil; ^1H NMR (400 MHz) δ : 6.28 (s, 1H), 4.15 (t, $J = 6.8$ Hz, 2H), 2.57 (t, $J = 7.6$ Hz, 2H), 1.67 – 1.60 (m, 4H), 1.42 – 1.38 (m, 2H), 1.30 – 1.28 (m, 10H), 0.94 (t, $J = 7.4$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz) δ : 164.4, 142.1, 119.3, 64.4, 43.5, 31.8, 30.6, 29.2, 29.1, 28.4, 28.0, 22.6, 19.2, 14.0, 13.7; IR (CH_2Cl_2): 1725, 1635 cm^{-1} ; LRMS (EI, 20 eV) m/z (%): 320 ($\text{M}^+ + 2$, 3), 318 (M^+ , 4), 265 (14), 263 (17), 239 ($\text{M}^+ - \text{Br}$, 100); HRMS (EI) for $\text{C}_{15}\text{H}_{27}^{79}\text{BrO}_2$ (M^+): calcd. 318.1195, found 318.1194.

(Z)-Isopropyl 3-bromoundec-2-enoate (6): Colorless oil; ^1H NMR (400 MHz) δ : 6.25 (s, 1H), 5.09 – 5.07 (m, 1H), 2.56 (t, $J = 8.0$ Hz, 2H), 1.64 – 1.60 (m, 2H), 1.28 (d, $J = 6.4$ Hz, 6H), 1.29 – 1.27 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz) δ : 163.8, 141.8, 119.6, 67.9, 43.5, 31.8, 29.2, 29.1, 28.4, 28.0, 22.6, 21.8, 14.1; IR (CH_2Cl_2): 1720, 1636 cm^{-1} ; LRMS (EI, 20 eV) m/z (%): 306 ($\text{M}^+ + 2$, 1), 304 (M^+ , 2), 265 (15), 263 (18), 247 (31), 245 (34), 225 (26), 183 ($\text{M}^+ - \text{Br}$, 100); HRMS (EI) for $\text{C}_{14}\text{H}_{25}^{79}\text{BrO}_2$ (M^+): calcd. 304.1038, found 304.1038.

(Z)-Tert-butyl 3-bromoundec-2-enoate (7): Colorless oil; ^1H NMR (400 MHz) δ : 6.20 (s, 1H), 2.53 (t, $J = 8.4$ Hz, 2H), 1.62 – 1.58 (m, 2H), 1.50 (s, 9H), 1.33 – 1.24 (m, 10H), 0.88 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz) δ : 163.6, 140.5, 120.7, 81.1, 43.4, 31.8, 29.2, 29.1, 28.5, 28.2, 28.0, 22.6, 14.1; IR (CH_2Cl_2): 1721, 1635 cm^{-1} ; LRMS (EI, 20 eV) m/z (%): 320 ($\text{M}^+ + 2$, 2), 318 (M^+ , 3), 265 (99), 263 (100), 239 ($\text{M}^+ - \text{Br}$, 68); HRMS (EI) for $\text{C}_{15}\text{H}_{27}^{79}\text{BrO}_2$ (M^+): calcd. 318.1195, found 318.1196.

(Z)-Methyl 3-bromo-4,4-dimethylpent-2-enoate (8): Colorless oil; ^1H NMR (400 MHz) δ : 6.36 (s, 1H), 3.76 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz) δ : 165.4, 153.0, 116.8, 51.6,

41.1, 29.3; IR (CH₂Cl₂): 1733, 1629 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 222 (M⁺ + 2, 5), 220 (M⁺, 3), 191 (15), 189 (17), 153 (22), 142 (9), 141 (M⁺ - Br, 100); HRMS (EI) for C₈H₁₃⁷⁹BrO₂ (M⁺): calcd. 220.0099, found 220.0098.

(Z)-Isopropyl 3-bromo-4,4-dimethylpent-2-enoate (9): Colorless oil; ¹H NMR (400 MHz) δ: 6.30 (s, 1H), 5.12 – 5.80 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 6H), 1.25 (s, 9H); ¹³C NMR (100 MHz) δ: 164.5, 151.8, 117.6, 68.1, 41.0, 29.3, 21.8; IR (CH₂Cl₂): 1721, 1628 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 250 (M⁺ + 2, 18), 248 (M⁺, 16), 191 (46), 189 (51), 169 (M⁺ - Br, 44), 127 (100); HRMS (EI) for C₁₀H₁₇⁷⁹BrO₂ (M⁺): calcd. 248.0412, found 248.0416.

(Z)-Methyl 3-bromo-3-phenylacrylate (10):¹ Colorless oil; ¹H NMR (400 MHz) δ: 7.62 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.39 (m, 3H), 6.73 (s, 1H), 3.82 (s, 3H); ¹³C NMR (100 MHz) δ: 164.8, 139.3, 138.0, 130.7, 128.5, 128.1, 120.0, 51.7; IR (CH₂Cl₂): 1731, 1609 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 242 (M⁺ + 2, 52), 240 (M⁺, 53), 211 (29), 209 (30), 161 (M⁺ - Br, 100); HRMS (EI) for C₁₀H₉⁷⁹BrO₂ (M⁺): calcd. 239.9786, found 239.9797.

(Z)-Methyl 3-bromo-3-p-tolylacrylate (11): Colorless oil; ¹H NMR (400 MHz) δ: 7.53 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 3.80 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100 MHz) δ: 165.3, 141.3, 136.7, 129.5, 129.3, 128.3, 119.2, 52.0, 21.5; IR (CH₂Cl₂): 1730, 1609 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 256 (M⁺ + 2, 19), 254 (M⁺, 17), 175 (M⁺ - Br, 43), 120 (8), 119 (100); HRMS (EI) for C₁₁H₁₁⁷⁹BrO₂ (M⁺): calcd. 253.9943, found 253.9924.

(Z)-Butyl 3-bromo-3-p-tolylacrylate (12): Colorless oil; ¹H NMR (400 MHz) δ: 7.53 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 4.22 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 1.70 – 1.65 (m, 2H), 1.44 – 1.42 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz) δ:

164.7, 140.9, 137.7, 136.5, 129.2, 128.0, 119.4, 64.6, 30.7, 21.2, 19.2, 13.7; IR (CH₂Cl₂): 1724, 1608 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 298 (M⁺ + 2, 6), 296 (M⁺, 7), 242 (66), 240 (66), 225 (21), 223 (21), 161 (M⁺ - C₄H₈ - Br, 100); HRMS (EI) for C₁₄H₁₇⁷⁹BrO₂ (M⁺): calcd. 296.0412, found 296.0412.

(Z)-Isopropyl 3-bromo-3-p-tolylacrylate (13): Colorless oil; ¹H NMR (400 MHz) δ: 7.53 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 5.20 – 5.11 (m, 1H), 2.38 (s, 3H), 1.31 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (100 MHz) δ: 164.1, 140.8, 129.6, 129.2, 129.1, 128.0, 119.9, 68.2, 21.9, 21.2; IR (CH₂Cl₂): 1718, 1609 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 284 (M⁺ + 2, 19], 282 (M⁺, 22), 225 (23), 223 (25), 198 (20), 196 (22), 161 (M⁺ - C₃H₇ - Br, 48), 119 (100); HRMS (EI) for C₁₃H₁₅⁷⁹BrO₂ (M⁺): calcd. 282.0256, found 282.0259.

(Z)-Tert-butyl 3-bromo-3-p-tolylacrylate (14): Colorless oil; ¹H NMR (400 MHz) δ: 7.51 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.61 (s, 1H), 2.38 (s, 3H), 1.54 (s, 9H); ¹³C NMR (100 MHz) δ: 163.9, 140.5, 135.9, 129.1, 128.3, 128.0, 121.2, 64.2, 28.2, 21.2; IR (CH₂Cl₂): 1720, 1609 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 298 (M⁺ + 2, 6), 296 (M⁺, 7), 242 (99), 240 (100), 161 (M⁺ - C₄H₈ - Br, 60); HRMS (EI) for C₁₄H₁₇⁷⁹BrO₂ (M⁺): calcd. 296.0412, found 296.0411.

(Z)-Methyl 3-bromo-3-(4-nitrophenyl)acrylate (15): Pale yellow solid, m.p. 60-63 °C (uncorrected); ¹H NMR (400 MHz) δ: 8.28 (d, *J* = 8.8 Hz, 2H), 8.00 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H); ¹³C NMR (100 MHz) δ: 164.0, 147.7, 140.8, 137.1, 130.6, 126.2, 123.4, 52.9; IR (CH₂Cl₂): 1729, 1610 cm⁻¹; LRMS (EI, 20 eV) *m/z* (%): 287 (M⁺ + 2, 26), 285 (M⁺, 30), 206 (M⁺ - Br, 100); HRMS (EI) for C₁₀H₈⁷⁹BrNO₄ (M⁺): calcd. 284.9637, found 284.9639.

(Z)-Isopropyl 3-bromo-3-(4-nitrophenyl)acrylate (16): Pale yellow oil; ^1H NMR (400 MHz) δ : 8.27 (d, $J = 8.8$ Hz, 2H), 7.94 (s, 1H), 7.48 (d, $J = 8.8$ Hz, 2H), 5.12 – 5.09 (m, 1H), 1.28 (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (100 MHz) δ : 162.9, 147.6, 141.0, 137.6, 130.7, 125.4, 123.3, 69.9, 21.7; IR (CH_2Cl_2): 1720, 1608 cm^{-1} ; LRMS (EI, 20 eV) m/z (%): 315 ($\text{M}^+ + 2$, 25), 313 (M^+ , 29), 234 ($\text{M}^+ - \text{Br}$, 100); HRMS (EI) for $\text{C}_{12}\text{H}_{12}^{79}\text{BrNO}_4$ (M^+): calcd. 312.9950, found 312.9951.

(Z)-Methyl 3-bromo-3-(4-fluorophenyl)acrylate (17): Colorless oil; ^1H NMR (400 MHz) δ : 7.62 (dd, $J = 4.6, 4.8$ Hz, 2H), 7.09 (dd, $J = 8.4, 8.8$ Hz, 2H), 6.68 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz) δ : 165.2, 164.7, 136.6, 131.7, 130.2, 119.8, 115.7 (t, $J = 21.5$ Hz), 51.8; IR (CH_2Cl_2): 1728, 1605 cm^{-1} ; LRMS (EI, 20 eV) m/z (%): 260 ($\text{M}^+ + 2$, 48), 258 (M^+ , 49), 179 ($\text{M}^+ - \text{Br}$, 99), 123 (100); HRMS (EI) for $\text{C}_{10}\text{H}_8^{79}\text{BrFO}_2$ (M^+): calcd. 257.9692, found 257.9675.

(Z)-Methyl 3-chlorooct-2-enoate (18).² Colorless oil; ^1H NMR (400 MHz) δ : 6.00 (s, 1H), 3.70 (s, 3H), 2.42 (t, $J = 7.6$ Hz, 2H), 1.62 – 1.58 (m, 2H), 1.32 – 1.22 (m, 4H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz) δ : 164.4, 151.0, 115.7, 51.3, 41.2, 30.6, 26.8, 22.3, 13.8.

(Z)-Methyl 3-chloro-3-phenylacrylate (19).² Colorless oil; ^1H NMR (300 MHz) δ : 7.69 (d, $J = 8.1$ Hz, 2H), 7.43 – 7.40 (m, 3H), 6.55 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz) δ : 164.9, 137.6, 131.1, 128.7, 128.3, 127.6, 116.3, 52.0.

(D) References

- (1) Lu, X.; Zhu, G.; Ma, S. *Chin. J. Chem.* **1993**, *11*, 267.
- (2) Li, J.-H.; Jiang, H.-F.; Feng, A.-Q.; Jia, L.-Q. *J. Org. Chem.* **1999**, *64*, 5984.

(E) Spectra

(Z)-Methyl 3-bromooct-2-enoate (3)

(Z)-Methyl 3-bromooct-2-enoate (3)

(Z)-Methyl 3-bromoundec-2-enoate (4)

(Z)-Methyl 3-bromoundec-2-enoate (4)

(Z)-Butyl 3-bromoundec-2-enoate (5)

(Z)-Butyl 3-bromoundec-2-enoate (5)

(Z)-Isopropyl 3-bromoundec-2-enoate (6)

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7-9-4
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late Jul 9 2004 temp not used
solvent CDC13 gain 20
file exp 0
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it 2.000 alfa 6.600
pb 14808
ps 2000
pt 1.000 dp 11
ft 8 in n
tt 4 hs PROCESSING nm
fn not used
DISPLAY
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lof -207.1 wp 3088.1
lpr 54 rfl 44.3
pw 6.250 rfp -32.4
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PLOT
in 0 nm wc 250
im 46 vc 0
lpr 20772 th nm cdc ph 3
  
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(Z)-Isopropyl 3-bromoundec-2-enoate (6)

[illegible]

(Z)-Tert-butyl 3-bromoundec-2-enoate (7)

(Z)-Methyl 3-bromo-4,4-dimethylpent-2-enoate (8)

(Z)-Methyl 3-bromo-4,4-dimethylpent-2-enoate (8)

(Z)-Isopropyl 3-bromo-4,4-dimethylpent-2-enoate (9)

(Z)-Isopropyl 3-bromo-4,4-dimethylpent-2-enoate (9)

(Z)-Methyl 3-bromo-3-phenylacrylate (10)

(Z)-Methyl 3-bromo-3-phenylacrylate (10)

(Z)-Methyl 3-bromo-3-p-tolylacrylate (11)

(Z)-Methyl 3-bromo-3-p-tolylacrylate (11)

(Z)-Butyl 3-bromo-3-p-tolylacrylate (12)

(Z)-Butyl 3-bromo-3-p-tolylacrylate (12)

(Z)-Isopropyl 3-bromo-3-p-tolylacrylate (13)

(Z)-Isopropyl 3-bromo-3-p-tolylacrylate (13)

(Z)-Tert-butyl 3-bromo-3-p-tolylacrylate (14)

(Z)-Tert-butyl 3-bromo-3-p-tolylacrylate (14)

(Z)-Methyl 3-bromo-3-(4-nitrophenyl)acrylate (15)

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				ref	1	exp	10.00				
				1H	1.000	10.00					
				2H	2.000	10.00					
				3H	3.000	10.00					
				4H	4.000	10.00					
				5H	5.000	10.00					
				6H	6.000	10.00					
				7H	7.000	10.00					
				8H	8.000	10.00					
				9H	9.000	10.00					
				10H	10.000	10.00					
				11H	11.000	10.00					
				12H	12.000	10.00					
				13H	13.000	10.00					
				14H	14.000	10.00					
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				19H	19.000	10.00					
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				24H	24.000	10.00					
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				26H	26.000	10.00					
				27H	27.000	10.00					
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				30H	30.000	10.00					
				31H	31.000	10.00					
				32H	32.000	10.00					
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				34H	34.000	10.00					
				35H	35.000	10.00					
				36H	36.000	10.00					
				37H	37.000	10.00					
				38H	38.000	10.00					
				39H	39.000	10.00					
				40H	40.000	10.00					
				41H	41.000	10.00					
				42H	42.000	10.00					
				43H	43.000	10.00					
				44H	44.000	10.00					
				45H	45.000	10.00					
				46H	46.000	10.00

(Z)-Isopropyl 3-bromo-3-(4-nitrophenyl)acrylate (16)

(Z)-Isopropyl 3-bromo-3-(4-nitrophenyl)acrylate (16)

(Z)-Methyl 3-bromo-3-(4-fluorophenyl)acrylate (17)

(Z)-methyl 3-chlorooct-2-enoate (18)

(Z)-methyl 3-chlorooct-2-enoate (18)

(Z)-methyl 3-chloro-3-phenylacrylate (19)

(Z)-methyl 3-chloro-3-phenylacrylate (19)