SUPPORTING INFORMATION

Organic reactions in water: An efficient zinc mediated stereoselective synthesis of (*E*) and (*Z*)-trisubstituted alkenes using unactivated alkyl halides

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Experimental:

Spectra were recorded with the following instruments: ¹H NMR: Varian Gemini 200 MHz and ¹³C NMR: Varian Gemini 50 MHz; MS: VG Micromass 7070H (70eV); IR: Perkin-Elmer model 1310 spectrophotometer. Column chromatography was performed on silica gel (BDH 100-200 mesh) and TLC with silica gel GF₂₅₄. The spots were detected in an iodine chamber and under UV light.

Procedure for the synthesis

(2*E*)-Methyl-2-butyl-3-pentyl-propenoate 3dii: A suspension of methyl-3-acetoxy-2-methylene-octanoate **1d** (10 mM, 2.28 g), *n*-propyl iodide (50 mM, 4.9 mL) and Zn powder (40 mM, 2.6 g) in saturated aqueous NH₄Cl solution (20 mL) was stirred for 14 h at room temperature. After the reaction was completed (monitored by TLC), EtOAc (30 mL) was added and shaken. The organic layer was separated and the aqueous layer washed with EtOAc (3x20 mL). The combined organic portion was washed with brine (3x20 mL) followed by water (3x20 mL), dried over Na₂SO₄ filtered and concentrated. The residue was subjected to column chromatography over silica gel using 1% EtOAc in

hexane to afford (2*E*)-methyl-2-butyl-3-pentyl-propenoate **3dii** as a colorless liquid. Yield: 1.34 g. (63%).

IR (KBr): $\nu_{\max}$: 1716, 1644 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 6.70 (t, $J=7.0\text{Hz}$, 1H), 3.84 (s, 3H), 2.25 (t, $J=7.0$ Hz, 2H), 2.20-2.12 (m, 2H), 1.52-1.26 (m, 10H), 0.95-0.82 (m, 6H). ^{13}C NMR (50MHz, CDCl_3) : δ 168.6, 142.8, 132.4, 51.5, 31.8, 31.58, 29.7, 28.5, 26.7, 22.7, 22.5, 13.9, MS(EI): m/z 212. Anal. Calcd. for $\text{C}_{13}\text{H}_{24}\text{O}_2$: C, 73.53; H, 11.39. Found : C, 73.55; H, 11.40%.

(2*E*)-2-butyloct-2-en-1-ol (5): To a solution of LAH (7.5 mM, 285 mg) in dry THF (5 mL) was added anhydrous AlCl_3 (2.5 mM, 333 mg) in dry THF (3 mL) at 0°C . After stirring for 30 min at the same temperature **3dii** (5 mM, 1.06g) in dry THF (10 mL) was added, stirred it for 2 hour and allowed to come at room temperature. Excess hydride was decomposed by the cautious dropwise addition of 5mL saturated aqueous Na_2SO_4 solution. The etherial solution was then separated and aqueous layer was washed with ether (3x15mL). Combined etherial portion was dried and filtered using a celite filter pad concentrated under low pressure. The residue was column chromatographed over silica gel using 7% EtOAc in hexane to afford the alcohol **5** in pure form. Yield: 0.848 g (92%)

IR (KBr): $\nu_{\max}$ 3341 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 5.37 (t, $J = 7.0$ Hz, 1H), 3.98 (s, 2H), 2.12-1.91 (m, 3H), 1.50-1.16 (m, 11H), 0.89 (m, 6H): ^{13}C NMR (50MHz, CDCl_3) : δ 139.2, 127.1, 67.2, 31.7, 30.9, 29.5, 27.7, 27.5, 22.8, 22.6, 14.1. MS(EI): m/z 184. Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{O}_2$. C, 78.26; H, 13.04. Found: C, 78.22; H, 13.07%

(2*E*)-2-butyloct-2-enal 6: To a stirred suspension of pyridinium dichromate (PDC) (4.5 mM, 1.69 g) in dry CH_2Cl_2 (5 mL) was added the alcohol **5** (3 mM, 0.552 g) in dry CH_2Cl_2 with catalytic amount (2 drops) of Ac_2O and a pinch of molecular sieves (4 Å) powder at room temperature. After 3 h dry ether (10 mL) was added and the supernatant liquid was decanted from the black gum. The insoluble residue was washed thoroughly with dry ether (2x5 mL). The combined organic solution was passed through a short column containing silica gel. Removal of the solvent gave a colorless liquid which on

column chromatography over silica gel using 1%EtOAc in hexane afforded the aldehyde **6** in pure form. Yield: 0.475 g (87%)

IR (KBr): $\nu_{\max}$ 1688, 1640 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 9.36 (s, 1H), 6.42 (t, $J = 7.0$ Hz, 1H), 2.52-2.18 (m, 4H), 1.72-1.12 (m, 10H), 0.85 (m, 6H); ^{13}C NMR (50MHz, CDCl_3) : δ 195.2, 155.1, 143.7, 31.5, 31.0, 28.8, 28.3, 23.7, 22.6, 22.5, 13.8.; MS(EI): m/z 182. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.12; H, 12.08. Found: C, 79.09; H, 12.10%.

The analytical and spectral data of the prepared compounds are given below. All the compounds were obtained as colorless oil.

3 a i (E) : (2E)-Methyl-2-pentyl-3-phenyl-propenoate :

IR (KBr): $\nu_{\max}$ 1714, 1631, 1447, 1200 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 7.62 (s, 1H), 7.42-7.20 (m, 5H), 3.80 (s, 3H), 2.44 (t, $J = 7.0$ Hz, 2H), 1.62-1.20 (m, 6H), 0.84 (t, $J = 7.0$ Hz, 3H); MS(EI) : m/z 232, Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.59; H, 86.21. Found :C, 77.42; H, 86. 34%.

3 a ii (E) : (2E)-Methyl-2-heptyl-3-phenyl-propenoate :

^1H NMR (200 MHz, CDCl_3) : δ 7.75 (s, 1H), 7.58-7.40 (m, 5H), 3.92 (s, 3H), 2.62 (t, $J = 7.0$ Hz, 2H), 1.74-1.32 (m, 10H), 0.99 (t, $J = 7.0$ Hz, 3H); MS(EI) : m/z 260, Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: C, 78.46; H, 9.23. Found :C, 78.55; H, 9.41%.

3 a iii (E) : (2E)-Methyl-2-isobutyl-3-phenyl-propenoate :

^1H NMR (200 MHz, CDCl_3) : δ 7.68 (s, 1H), 7.42-7.22 (m, 5H), 3.78(s, 3H), 2.44 (d, $J = 7.0$ Hz, 2H), 1.84 (m, 1H), 0.82 (d, $J = 7.0$ Hz, 6H); MS(EI) : m/z 218, Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: C, 77.06; H, 8.26. Found :C, 77.24; H, 8.13%.

3 b i (E) : (2E)-Methyl-3-(2'-chlorophenyl)-2-pentyl-propenoate :

^1H NMR (200 MHz, CDCl_3) : δ 7.64 (s, 1H), 7.42 (dd, $J=8.0, 1.5$ Hz, 1H), 7.30-7.22 (m, 3H), 3.84 (s, 3H), 2.36 (t, $J=7.0$ Hz, 2H), 1.54-1.20 (m, 6H),

0.92 (t, $J = 7.0$ Hz, 3H); MS(EI) : m/z 266 and 268, Anal. Calcd for $C_{15}H_{19}ClO_2$: C, 67.67; H, 7.14. Found : C, 67.38; H, 7.02%.

3 b ii (E) : (2E)-Methyl-3-(2'-chlorophenyl)-2-heptyl-propenoate :

1H NMR (200 MHz, $CDCl_3$) : δ 7.66 (s, 1H), 7.42 (dd, $J=8.0, 1.5$ Hz, 1H), 7.28-7.16 (m, 3H), 3.84 (s, 3H), 2.45 (t, $J=7.0$ Hz, 2H), 1.62-1.20 (m, 10H), 0.92 (t, $J = 7.0$ Hz, 3H); MS(EI) : m/z 294 and 296, Anal. Calcd for $C_{17}H_{23}ClO_2$: C, 69.36; H, 7.82. Found : C, 68.98; H, 7.67%.

3 b iii (E) : (2E)-Methyl-3-(2'-chlorophenyl)-2-isobutyl-propenoate :

IR (KBr) : ν_{max} 1721, 1464, 1439, 1227 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) : δ 7.68 (s, 1H), 7.40 (dd, $J=8.0, 1.5$ Hz, 1H), 7.29-7.18 (m, 3H), 3.82 (s, 3H), 2.32 (d, $J=7.0$ Hz, 2H), 1.78 (m, 1H), 0.78 (d, $J = 7.0$ Hz, 6H); MS(EI) : m/z 252 and 254, Anal. Calcd for $C_{14}H_{17}ClO_2$: C, 66.67; H, 6.75. Found : C, 66.43; H, 6.62%.

3 c i (E) : (2E)-Methyl-3-(4'-methoxyphenyl)-2-propyl-propenoate :

1H NMR (200 MHz, $CDCl_3$) : δ 7.59 (s, 1H), 7.30 (d, $J=8.0$ Hz, 2H), 7.30 (d, $J=8.0$ Hz, 2H), 6.88 (d, $J=8.0$ Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 2.48 (t, $J=7.0$ Hz, 2H), 1.64-1.44 (m, 2H), 0.98 (t, $J = 7.0$ Hz, 3H); MS(EI) : m/z 234, Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.80; H, 7.69. Found : C, 71.72; H, 7.51%.

3 c ii (E) : (2E)-Methyl-3-(4'-methoxyphenyl)-2-pentyl-propenoate :

IR (KBr) : ν_{max} 1709, 1606, 1511, 1438, 1251 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) : δ 7.58 (s, 1H), 7.28 (d, $J=8.0$ Hz, 2H), 6.84 (d, $J=8.0$ Hz, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 2.48 (t, $J=7.0$ Hz, 2H), 1.62-1.22 (m, 6H), 0.96 (t, $J=7.0$ Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) : δ 169.1, 159.8, 138.3, 131.7, 130.9, 128.3, 114.0, 55.2, 51.7, 31.9, 28.8, 27.5, 22.4, 13.9. MS(EI): m/z 262. Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.28, H, 8.40. Found: C, 73.37; H, 8.32%.

3 c iii (E) : (2E)-Methyl-2-isobutyl-3-(4'-methoxyphenyl)-propenoate :

^1H NMR (200 MHz, CDCl_3) : δ 7.64 (s, 1H), 7.39 (d, $J=8.0\text{Hz}$, 2H), 6.90 (d, $J=8.0\text{Hz}$, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 2.52 (d, $J=7.0\text{ Hz}$, 2H), 1.92 (m, 1H), 0.94 (d, $J=7.0\text{ Hz}$, 6H). MS(EI): m/z 248. Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_3$: C, 72.58, H, 8.07. Found: C, 72.67; H, 8.02%.

3 d i (E) : (2E)-Methyl-3-pentyl-2-propyl-propenoate :

IR (KBr) : ν_{max} 1719, 1641, 1461, 1264, 1220 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 6.72 (t, $J=7.0\text{Hz}$, 1H), 3.74(s, 3H), 2.08 (t, $J=7.0\text{ Hz}$, 2H), 2.20-2.16(m, 2H), 1.58-1.16(m, 8H), 0.99-0.80 (m, 6H). ^{13}C NMR (50MHz, CDCl_3) : δ 169.0, 143.4, 132.5, 51.7, 32.3, 32.0, 30.1, 29.1, 28.9, 22.9, 14.3, MS(EI): m/z 198. Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_2$: C, 72.73; H, 11.11. Found : C, 72.58; H, 11.24%.

3 d ii (E) : (2E)-Methyl-2-butyl-3-pentyl-propenoate :

IR (KBr): ν_{max} : 1716, 1644 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 6.70 (t, $J=7.0\text{Hz}$, 1H), 3.84 (s, 3H), 2.25 (t, $J=7.0\text{ Hz}$, 2H), 2.20-2.12 (m, 2H), 1.52-1.26 (m, 10H), 0.95-0.82 (m, 6H). ^{13}C NMR (50MHz, CDCl_3) : δ 168.6, 142.8, 132.4, 51.5, 31.8, 31.58, 29.7, 28.5, 26.7, 22.7, 22.5, 13.9, MS(EI): m/z 212. Anal. Calcd. for $\text{C}_{13}\text{H}_{24}\text{O}_2$: C, 73.53; H, 11.39. Found : C, 73.55; H, 11.40%.

3 e i (E) : (2E)-Methyl-2,3-diisobutyl-propenoate :

IR (KBr) : ν_{max} 1716, 1643, 1461, 1256 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 6.70 (t, $J=7.0\text{Hz}$, 1H), 3.74(s, 3H), 2.28 (t, $J=7.0\text{ Hz}$, 2H), 2.02 (t, $J=7.0\text{Hz}$, 2H), 1.76-1.64 (m, 2H), 1.50-1.20 (m, 12H).; MS(EI): m/z 198. Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_2$: C, 72.72; H, 11.11. Found: C, 72.75; H, 11.09%.

3 e ii (E) : (2E)-Methyl-3-isobutyl-2-heptyl-propenoate :

^1H NMR (200 MHz, CDCl_3) : δ 6.70 (t, $J=7.0\text{Hz}$, 1H), 3.72 (s, 3H), 2.24 (t, $J=7.0\text{ Hz}$, 2H), 2.02 (t, $J=7.0\text{Hz}$, 2H), 1.74 (m, 1H), 1.39-1.20 (m, 10H), 0.94 (d, $J=7.0\text{Hz}$, 6H) 0.80 (t, $J=7.0\text{Hz}$, 3H). MS(EI): m/z 240. Anal. Calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_2$: C, 75.00; H, 11.67. Found : C, 74.82; H, 11.54%.

4 a i (Z) : (2Z)-2-pentyl-3-phenyl-propenenitrile:

^1H NMR (200 MHz, CDCl_3) : δ 7.68 (m, 2H), 7.43-7.32 (m, 3H), 6.90 (s, 1H), 2.42 (t, $J=7.0$ Hz, 2H), 1.72-1.61 (m, 2H), 1.42-1.30 (m, 4H), 0.92 (t, $J=7.0$ Hz, 3H). MS(EI): m/z 199. Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{N}$: C, 84.42; H, 8.54; N, 7.04. Found: C, 84.56; H, 8.62; N, 7.15%

4 a ii (Z) : (2Z)-2-heptyl-3-phenyl-propenenitrile:

^1H NMR (200 MHz, CDCl_3) : δ 7.70 (m, 2H), 7.44-7.30 (m, 3H), 6.85 (s, 1H), 2.40 (t, $J=7.0$ Hz, 2H), 1.71-1.58 (m, 2H), 1.41-1.18 (m, 8H), 0.86 (t, $J=7.0$ Hz, 3H). MS(EI): m/z 227. Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{N}$: C, 84.58; H, 7.25; N, 6.17; Found: C, 84.67; H, 7.36; N, 6.08%

4 a iii (Z) : (2Z)-2-isobutyl-3-phenyl-propenenitrile:

IR (KBr) : ν_{max} 2227, 1722, 1626, 1459, 1220 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 7.70 (dd, $J=8.0, 1.5$ Hz, 2H), 7.40-7.32 (m, 3H), 6.82 (s, 1H), 2.25 (d, $J=7.0$ Hz, 2H), 2.02 (m, 1H), 0.90 (d, $J=7.0$ Hz, 6H). ^{13}C NMR (50 MHz, CDCl_3): 144.3, 133.8, 129.9, 129.1, 128.8, 128.6, 118.9, 110.8, 45.4, 27.5, 21.9; MS(EI): m/z 185; Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}$: C, 84.32; H, 8.11; N, 7.57; Found :C, 84.47; H, 8.03; N, 7.44%

4 b i (Z) : (2Z)-3-(2'-chlorophenyl)-2-pentyl-propenenitrile:

IR (KBr) : ν_{max} 2367, 2034, 1728, 1636, 1440, 1220 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) : δ 7.89 (d, $J=8.0$ Hz, 1H), 7.50 (dd, $J=8.0, 1.5$ Hz, 1H), 7.42-7.33 (m, 2H), 7.20 (s, 1H), 2.42 (t, $J=7.0$ Hz, 2H), 1.78-1.57 (m, 2H), 1.44-1.16 (m, 4H), 0.90 (t, $J=7.0$ Hz, 3H). MS(EI): m/z 233 and 235; Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{ClN}$: C, 72.10; H, 6.87; N, 6.00; Found: C, 72.28; H, 6.93; N, 5.89%

4 b ii (Z) : (2Z)-3-(2'-chlorophenyl)-2-heptyl-propenenitrile:

^1H NMR (200 MHz, CDCl_3) : δ 7.92 (d, $J=8.0$ Hz, 1H), 7.42 (dd, $J=8.0, 1.5$ Hz, 1H), 7.38-7.30 (m, 2H), 7.19 (s, 1H), 2.44 (t, $J=7.0$ Hz, 2H), 1.74-1.60 (m, 2H), 1.40-1.22 (m, 8H), 0.86 (t, $J=7.0$ Hz, 3H). MS(EI): m/z 261 and 263;

Anal. Calcd for C₁₆H₂₀ClN: C, 73.56; H, 7.66; N, 5.36; Found: C, 73.42; H, 7.78; N, 5.42%

4 b iii (Z) : (2Z)-3-(2'-chlorophenyl)-2-isobutyl-propenenitrile:

¹H NMR (200 MHz, CDCl₃) : δ 7.96 (d, *J*=8.0Hz, 1H), 7.42 (dd, *J*=8.0, 1.5Hz, 1H), 7.38-7.20 (m, 2H), 7.16 (s, 1H), 2.38 (d, *J*=7.0 Hz, 2H), 2.02 (m, 1H), 0.98 (d, *J*=7.0Hz, 6H). MS(EI): *m/z* 219 and 221; Anal. Calcd for C₁₃H₁₄ClN: C, 71.23; H, 6.39; N, 6.39; Found: C, 70.92; H, 6.46; N, 6.33%

4 c i (Z) : (2Z)-2-pentyl-3-propyl-propenenitrile:

IR (KBr) : ν_{max} 2215, 1461, 1352, 1219 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) : δ 6.04 (t, *J*=7.0Hz, 1H), 2.22-2.02 (m, 4H), 1.45-1.12 (m, 8H), 1.02-0.84 (m, 6H). MS(EI): *m/z* 165. Anal. Calcd. for C₁₁H₁₉N: C, 80.00; H, 11.52; N, 8.49. Found: C, 79.82; H, 11.43; N, 8.57%.

4 c ii (Z) : (2Z)-2-heptyl-3-propyl-propenenitrile:

¹H NMR (200 MHz, CDCl₃) : δ 6.03 (t, *J*=7.0Hz, 1H), 2.22-2.03 (m, 4H), 1.43-1.20 (m, 12H), 1.02-0.84 (m, 6H). MS(EI): *m/z* 193. Anal. Calcd. for C₁₃H₂₃N: C, 79.79; H, 11.92; N, 7.25. Found: C, 79.90; H, 11.81; N, 7.32%.