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Supporting Information for

Facile Synthesis of α -Substituted Acrylate Esters

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2,2-Dimethyl-5-phenethyl-[1,3]dioxane-4,6-dione (7b). White solid (94% yield): mp 98–99 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.74 (s, 3H), 1.76 (s, 3H), 2.37-2.46 (m, 2H), 2.82-2.89 (m, 2H), 3.48 (t, *J* = 5.3 Hz, 1H), 7.18-7.34 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 26.5, 27.9, 28.4, 32.3, 45.0, 104.8, 126.3, 128.5, 128.6, 140.3, 165.4. Anal. Calcd for C₁₄H₁₆O₄: C, 67.73; H, 6.50. Found: C, 67.54; H, 6.52.

2,2-Dimethyl-5-(3-phenyl-propyl)-[1,3]dioxane-4,6-dione (7c). Colorless oil (68% yield): ¹H NMR (400 MHz, CDCl₃) δ 1.73 (s, 6H), 1.76-1.85 (m, 2H), 2.13-2.20 (m, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 3.48 (t, *J* = 5.1 Hz, 1H), 7.15-7.33 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 26.1, 26.6, 27.9, 28.3, 35.7, 45.9, 104.8, 125.9, 123.8, 123.9, 141.4, 165.4. Anal. Calcd for C₁₅H₁₈O₄: C, 68.69; H, 6.92. Found: C, 68.83; H, 6.98.

5-(3,3-Dimethyl-butyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (7d). White solid (78% yield): mp 65–66 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (s, 9H), 1.28-1.34 (m, 2H), 1.76 (s, 3H), 1.79 (s, 3H), 2.06-2.14 (m 2H), 3.53 (t, *J* = 4.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 26.9, 28.4, 29.0, 30.3, 40.0, 46.4, 104.7, 165.6. Anal. Calcd for C₁₂H₂₀O₄: C, 63.14; H, 8.83. Found: C, 62.95; H, 8.79.

2,2-Dimethyl-5-(3-tritylsulfanyl-propyl)-[1,3]dioxane-4,6-dione (7e). White solid (75% yield): mp 129–130 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.56-1.65 (m, 2H), 1.69 (s, 3H), 1.71 (s, 1H), 1.99-2.06 (m, 2H), 2.22 (t, *J* = 7.3 Hz, 2H), 3.34 (t, *J* = 5.3 Hz, 1H), 7.15-7.43 (m, 15H); ¹³C NMR (100 MHz, CDCl₃) δ 26.1, 26.3, 26.9, 28.6, 31.8, 46.0, 67.0, 104.7, 126.6, 127.9, 129.7, 145.1, 165.1. Anal. Calcd for C₂₈H₂₈SO₄: C, 73.02; H, 6.13; S, 6.96. Found: C, 73.12; H, 6.19; S, 6.90.

(*R*)-2-*tert*-Butoxycarbonylamino-5-(2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-pentanoic acid *tert*-butyl ester (7h). White solid (80% yield): mp 106–107 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.41 (s, 9H), 1.44 (s, 9H), 1.73 (s, 3H), 1.77 (s, 3H), 1.40-1.90 (m, 4H), 2.00-2.20 (m, 2H), 3.53 (t, *J* = 5.0 Hz, 1H), 4.10-4.20 (m, 1H), 5.04 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 22.2, 26.0, 26.7, 27.9, 28.3, 28.4, 32.8, 45.9, 53.5, 80.0, 82.0, 104.9, 155.3, 165.3, 171.7; Anal. Calcd for C₂₀H₃₃NO₈: C, 57.82; H, 8.01; N, 3.37. Found: C, 57.96; H, 8.03; N, 3.31.

2-Phenethyl-acrylic acid methyl ester (8b). Colorless oil (91% yield): ^1H NMR (400 MHz, CDCl_3) δ 2.58-2.65 (m, 2H), 2.75-2.83 (m, 2H), 3.76 (s, 3H), 5.51 (s, 1H), 6.16 (s, 1H), 7.15-7.33 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 33.7, 34.7, 51.6, 125.2, 125.8, 128.2, 128.3, 139.6, 141.2, 167.4. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.53.

2-(3-Phenyl-propyl)-acrylic acid methyl ester (8c). Colorless oil (84% yield): ^1H NMR (300 MHz, CDCl_3) δ 1.75-1.88 (m, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 2.64 (t, $J = 7.7$ Hz, 2H), 3.75 (s, 3H), 5.54 (s, 1H), 6.16 (s, 1H), 7.15-7.33 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 29.9, 31.4, 35.2, 51.6, 124.7, 125.7, 128.2, 128.3, 140.2, 141.9, 167.5. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C, 76.44; H, 7.90. Found: C, 76.42; H, 7.88.

2-(3,3-Dimethyl-butyl)-acrylic acid methyl ester (8d). Colorless oil (73% yield): ^1H NMR (400 MHz, CDCl_3) δ 0.92 (s, 9H), 1.30-1.35 (m, 2H), 2.24-2.30 (m, 2H), 3.75 (s, 3H), 5.53 (s, 1H), 6.11 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 27.1, 29.2, 30.3, 42.7, 51.7, 124.0, 141.5, 167.8. Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.55; H, 10.66. Found: C, 70.25; H, 10.64.

2-(3-Tritylsulfanyl-propyl)-acrylic acid methyl ester (8e). Colorless oil (98% yield): ^1H NMR (400 MHz, CDCl_3) δ 1.54 (quint., $J = 7.4$ Hz, 2H), 2.16 (t, $J = 7.3$ Hz, 2H), 2.24 (t, $J = 7.4$ Hz, 2H), 3.70 (s, 3H), 5.40 (s, 1H), 6.07 (s, 1H), 7.17-7.30 (m, 9H), 7.38-7.43 (6H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.2, 31.1, 31.3, 51.7, 66.5, 125.2, 126.5, 127.8, 129.5, 139.5, 144.9, 167.4. Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{SO}_2$: C, 77.58; H, 6.81; S, 7.97. Found: C, 77.42; H, 6.60; S, 7.79.

2-(2-tert-Butoxycarbonylamino-3-methyl-butyl)-acrylic acid methyl ester (8f). White solid (83% yield): mp 57-58 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 0.89 (d, $J = 6.8$ Hz, 3H), 0.91 (t, $J = 6.8$ Hz, 3H), 1.40 (s, 9H), 1.73-1.80 (m, 1H), 2.20 (dd, $J = 10.6, 14.2$ Hz, 1H), 2.51 (dd, $J = 3.4$ Hz, 14.2 Hz, 1H), 3.62-3.70 (m, 1H), 3.74 (s, 3H), 4.36 (d, $J = 9.6$ Hz, 1H), 5.62 (s, 1H), 6.20 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7, 19.0, 28.3, 32.3, 34.7, 51.9, 55.0, 78.8, 126.8, 137.7, 155.8, 167.8. Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_4$: C, 61.97; H, 9.29; N, 5.16. Found: C, 62.07; H, 9.31; N, 5.21.

2-(2-*tert*-Butoxycarbonylamino-3-phenyl-propyl)-acrylic acid methyl ester (8g). White solid (82% yield): mp 94-95 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.37 (s, 9H), 2.27-2.42 (m, 1H), 2.53-2.60 (m, 1H), 2.75-2.92 (m, 2H), 3.74 (s, 3H), 3.9-4.05 (m, 1H), 4.45-4.53 (m, 1H), 5.58 (s, 1H), 6.21 (s, 1H), 7.15-7.33 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 28.3, 36.5, 41.3, 51.2, 51.9, 79.0, 126.3, 127.4, 128.3, 129.4, 137.2, 137.9, 155.3, 167.7; Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_4 \cdot 0.23 \text{H}_2\text{O}$: C, 66.92; H, 7.80; N, 4.34. Found: C, 66.92; H, 7.74; N, 4.47.

(*R*)-2-*tert*-Butoxycarbonylamino-6-methylene-heptanedioic acid 1-*tert*-butyl ester 7-methyl ester (8h). Colorless oil (80% yield): ^1H NMR (300 MHz, CDCl_3) δ 1.41 (s, 9H), 1.43 (s, 9H), 1.45-1.83 (m, 4H), 2.21-2.38 (m, 2H), 3.72 (s, 3H), 4.20-4.45 (m, 1H), 5.02 (d, $J = 7.8$ Hz, 1H), 5.50 (s, 1H), 6.13 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.9, 28.0, 28.3, 31.4, 32.4, 51.7, 53.7, 79.5, 81.7, 125.1, 140.0, 155.3, 167.5, 171.9. Anal. Calcd for $\text{C}_{18}\text{H}_{31}\text{NO}_6$: C, 60.48; H, 8.74; N, 3.92. Found: C, 60.35; H, 8.58; N, 3.80.

2-Phenyl-acrylic acid methyl ester (8i). Colorless oil (72% yield): ^1H NMR (400 MHz, CDCl_3) δ 3.77 (s, 3H), 5.85 (s, 1H), 6.33 (s, 1H), 7.27-7.34 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 51.9, 126.7, 127.9, 128.0, 128.1, 136.5, 141.1, 167.0. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.06; H, 6.21. Found: C, 73.62; H, 6.30.