**Mild α -Halogenation Reactions
of 1,3-Dicarbonyl Compounds Catalyzed by Lewis Acids**

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Supporting Information

Characterization data of compounds **2b**, **2e**, **4b**, **4d**, **4e**, **5b**, **7a**, and **7c**. ^1H NMR and ^{13}C NMR spectra of compounds **2b**, **2d**, **2e**, **4b**, **4d**, **4e**, **5b**, **7a**, and **7c**.

Characterization data:

Compound 2b: A light yellow oil; analytical TLC (silic gel 60), 10% EtOAc in *n*-hexane, $R_f = 0.47$; ^1H NMR (300 MHz, CDCl_3) δ 5.38 – 5.49 (m, 1H), 5.24 – 5.33 (m, 1H), 4.27 (q, $J = 7.3$ Hz, 2H), 2.84 – 2.95 (m, 1H), 2.68 – 2.80 (m, 1H), 2.28 – 2.41 (m, 2H), 2.04 – 2.14 (m, 2H), 1.98 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H), 0.96 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 ; DEPT) δ 200.5 (C), 168.6 (C), 133.5 (CH), 126.9 (CH), 63.4 (CH₂), 63.2 (C), 38.5 (CH₂), 25.7 (CH₃), 22.6 (CH₂), 20.8 (CH₂), 14.5 (CH₃), 14.2 (CH₃); IR (CH_2Cl_2) 2967, 1759, 1725 cm^{-1} ; LRMS for $\text{C}_{12}\text{H}_{19}\text{BrO}_3$ (EI, 20 eV) m/z 291 ($\text{M}^+ - \text{H}$, 5), 289 ($\text{M}^+ - \text{H}$, 2), 211 (64), 165 (100); HRMS (EI) for $\text{C}_{12}\text{H}_{19}\text{BrO}_3$ (M^+): calcd 290.0518, found 290.0520.

Compound 2e: A light yellow oil; analytical TLC (silic gel 60), 30% EtOAc in *n*-hexane, $R_f = 0.44$; ^1H NMR (400 MHz, CDCl_3) δ 5.07 – 5.13 (m, 1H), 4.37 – 4.47 (m, 2H), 3.14 – 3.27 (m, 2H), 3.00 (m, 1H), 2.52 (m, 1H), 2.30 (q, $J = 7.3$ Hz, 2H), 1.68 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; DEPT) δ 199.6 (C), 170.8 (C), 133.7 (C), 122.3 (CH), 66.2 (CH₂), 57.0 (C), 38.8 (CH₂), 36.1 (CH₂), 27.4 (CH₃), 24.5 (CH₂), 18.0 (CH₃); IR (CH_2Cl_2) 2919, 1780, 1717 cm^{-1} ; LRMS for $\text{C}_{11}\text{H}_{15}\text{BrO}_3$ (EI, 20 eV) m/z 275 ($\text{M}^+ - \text{H}$, 3), 273 ($\text{M}^+ - \text{H}$, 4), 196 (18), 195 (78), 113 (100); HRMS (EI) for $\text{C}_{11}\text{H}_{15}\text{O}_3$ ($\text{M}^+ - \text{Br}$): calcd 195.1021, found 195.1020;

Compound 4b: A light yellow oil; analytical TLC (silic gel 60), 10% EtOAc in *n*-hexane, $R_f = 0.35$; ^1H NMR (300 MHz, CDCl_3) δ 12.8 (s, $0.1 \times 1\text{H}$, enol), 5.04 – 5.09 (m, 1H), 4.37 (s, $0.9 \times 1\text{H}$), 4.26 (q, $J = 7.2$ Hz, 2H), 2.78 (dt, $J = 7.3, 2.3$ Hz, $0.8 \times 2\text{H}$), 2.55 – 2.60 (m, $0.2 \times 2\text{H}$), 2.31 (q, $J = 7.2$ Hz, 2H), 1.68 (s, 3H), 1.62 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 ; DEPT) δ 198.4 (C), 165.2 (C), 133.5 (CH), 121.9

(CH), 63.1 (CH₂), 49.3 (CH), 39.3 (CH₂), 25.7 (CH₃), 22.6 (CH₂), 17.7 (CH₃), 13.9 (CH₃); IR (CH₂Cl₂) 2977, 2936, 1740, 1721 cm⁻¹; LRMS for C₁₁H₁₇BrO₃ (EI, 20 eV) *m/z* 277 (M⁺ – H, 13), 275 (M⁺ – H, 11), 197 (42), 151 (100), 115 (65); HRMS (EI) for C₁₁H₁₇BrO₃ (M⁺) calcd 276.0361, found 276.0352.

Compound 4d:

Compound 4d

A light yellow oil; analytical TLC (silic gel 60), 40% EtOAc in *n*-hexane, *R_f* = 0.43; ¹H NMR (300 MHz, CDCl₃) δ 7.22 – 7.43 (m, 5H), 6.77 – 6.90 (m, 1H), 5.87 – 6.02 (m, 1H), 4.49 – 5.09 (m, 3H), 3.92 – 4.38 (m, 6H), 1.23 – 1.36 (m, 6H); ¹³C NMR (75 MHz, CDCl₃; DEPT) δ 165.0 (C), 165.6 (C), 164.6 (C), 164.5 (C), 141.4 (CH), 141.4 (CH), 136.1 (C), 135.1 (C), 129.5 (CH), 129.1 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 126.9 (CH), 123.7 (CH), 123.3 (CH), 63.8 (CH₂), 63.8 (CH₂), 61.1 (CH₂), 60.8 (CH₂), 52.1 (CH₂), 49.5 (CH₂), 48.3 (CH₂), 47.0 (CH₂), 42.5 (CH), 42.4 (CH), 14.5 (CH₃), 14.2 (CH₃); IR (CH₂Cl₂) 2977, 1764, 1719, 1662 cm⁻¹; LRMS for C₁₈H₂₂BrNO₅ (EI, 20 eV) *m/z* 413 (M⁺, 2), 411 (M⁺, 2), 332 (19), 286 (38), 218 (100); HRMS (EI) for C₁₈H₂₂BrNO₅ (M⁺) calcd 411.0681, found 411.0675.

Compound 4e: A colorless oil; analytical TLC (silic gel 60), 50% EtOAc in *n*-hexane, *R_f* = 0.48; ¹H NMR (400 MHz, CDCl₃) δ 5.44 – 5.51 (m, 1H), 5.31 – 5.39 (m, 1H), 4.98 (s, 1H), 3.09 (s, 3H), 3.00 (s, 3H), 2.71 – 2.87 (m, 2H), 1.69 – 2.04 (m, 4H), 1.69 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃; DEPT) δ 200.5 (C), 165.5

(C), 133.4 (CH), 128.3 (CH), 49.0 (CH), 39.0 (CH₂), 38.4 (CH₃), 36.6 (CH₃), 31.9 (CH₂), 25.8 (CH₂), 24.1 (CH₂), 14.2 (CH₃); IR (CH₂Cl₂) 2964, 2942, 1740, 1714, 1654 cm⁻¹; LRMS for C₁₂H₂₀BrNO₂ (EI, 20 eV) *m/z* 210 (M⁺ – Br, 100), 165 (14), 129 (44), 113 (13); HRMS (EI) for C₁₂H₂₀NO₂ (M⁺ – Br) calcd 210.1494, found 210.1505.

Compound 5b: A light yellow oil; analytical TLC (silic gel 60), 10% EtOAc in *n*-hexane, *R_f* = 0.42; ¹H NMR (300 MHz, CDCl₃) δ 5.10 (tq, *J* = 7.2, 1.3 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.38 (q, *J* = 7.3 Hz, 2H), 1.69 (s, 3H), 1.64 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.3, 163.8, 133.7, 121.7, 64.7, 60.1, 36.2, 25.7, 23.7, 17.7, 13.7; IR (CH₂Cl₂) 2974, 1753, 1739 cm⁻¹; LRMS for C₁₁H₁₆Br₂O₃ (EI, 20 eV) *m/z* 277 (M⁺ – Br, 17), 275 (M⁺ – Br, 17), 197 (54), 151 (100), 115 (68); HRMS (EI) for C₁₁H₁₆BrO₃ (M⁺ – Br) calcd 275.0283, found 275.0275.

Compound 7a: A colorless liquid; analytical TLC (silica gel 60), 10% EtOAc in *n*-hexane, *R_f* = 0.32; ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.22 (m, 5H), 4.23 – 4.20 (m, 2H), 3.73 (d, *J* = 14.5 Hz, 1H), 3.58 (d, *J* = 14.5 Hz, 1H), 2.52 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.0, 168.2, 136.2, 130.2, 128.2, 127.4, 63.2, 54.3, 44.2, 26.2, 13.7; IR (CH₂Cl₂) 2984, 1659 cm⁻¹; LRMS for C₁₃H₁₅IO₃ (EI, 20 eV) *m/z* 219 (M⁺ – I, 45), 220 (M⁺ – I, 22), 177 (100); HRMS (EI) for C₁₃H₁₅O₃ (M⁺ – I): calcd 219.1021, found 219.1023.

Compound 7c: A colorless liquid; analytical TLC (silica gel 60), 10% EtOAc in *n*-hexane, *R_f* = 0.33; ¹H NMR (400 MHz, CDCl₃) δ 4.31 – 4.25 (m, 2H), 2.47 (s, 3H), 2.23 – 2.17 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.1, 168.6, 63.1, 56.4, 32.3, 25.8, 13.8, 12.1; IR (CH₂Cl₂) 1742, 1713,

2979 cm^{-1} ; LRMS for $\text{C}_8\text{H}_{13}\text{IO}_3$ (EI, 20 eV) m/z 156 ($\text{M}^+ - \text{I}$, 37), 128 (100), 127 (62);

HRMS for $\text{C}_8\text{H}_{13}\text{O}_3$ ($\text{M}^+ - \text{I}$): calcd 157.0865, found 157.0869.