**Ytterbium Triflate Promoted Tandem One-pot Oxidation-Intramolecular Cannizzaro
Reaction of Aryl Methyl Ketones**

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Supporting Information

General: Purchased reagents and solvents were used as received without further purification. Aryl glyoxals were prepared as described in the literature.¹³ Thin-layer chromatography (TLC) was performed on precoated silica gel aluminium plates and components were visualized by observation under UV light or by treating plates with a solution of phosphomolibdic acid (7% in ethanol) followed by heating. Column chromatography was performed on 230-400 mesh silica gel. ¹H NMR spectra were recorded at 200 MHz in a Bruker DPX apparatus; ¹³C NMR spectra were recorded at 50.32 MHz using the same apparatus. The following abbreviations are used to indicate multiplicity: s, singlet; d, doublet; m, multiplet; br s, broad signal.

Cannizzaro Reaction of Aryl Glyoxals. General Procedure.

To a solution of aryl glyoxal hydrate (1.0 mmol) in 2-propanol (3 mL), Yb(OTf)₃ hydrate (0.1 mmol) was added and the resulting mixture was stirred at 80°C for 18 h. This solution was diluted with H₂O (20 mL) and extracted with AcOEt (3 x 10 mL). The combined organic phases were dried on Na₂SO₄, the solvent removed under reduced pressure and the residue purified by SiO₂ gel column chromatography, eluent CH₂Cl₂, yielding the desired α -hydroxy esters.

Isopropyl hydroxy(phenyl)acetate (2): 80% yield. Analytical and spectroscopic data are identical to those reported in the literature.⁷ Anal. Calcd. for C₁₁H₁₄O₃: C, 68.02; H, 7.27. Found: C, 68.04; H, 7.25.

Isopropyl hydroxy(4-nitrophenyl)acetate (4): 99% yield. White solid; m.p. 65 - 67 °C; IR (cm⁻¹) 3500 (br), 1732, 1524, 1348; ¹H NMR δ 1.15 (d, 3H, *J* = 6.2 Hz), 1.32 (d, 3H, *J* = 6.2

Hz), 3.94 (s br, 1H), 5.22 (set, 1H, $J = 6.2$ Hz), 5.28 (s, 1H), 7.65 - 8.44 (m, 4H); ^{13}C NMR δ 21.3, 21.6, 71.1, 72.0, 123.8, 127.3, 142.4, 155.3, 171.9; exact mass m/z calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_5$ 237.100108, found 237.100105. Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{NO}_5$: C, 55.23; H, 5.48. Found: C, 55.20; H, 5.47.

Isopropyl hydroxy(4-methylphenyl)acetate (6): 80% yield. Analytical and spectroscopic data are identical to those reported in the literature.⁷ Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_3$: C, 69.21; H, 7.74. Found: C, 69.19.20; H, 7.76.

Isopropyl hydroxy(4-chlorophenyl)acetate (8): 70% yield. Analytical and spectroscopic data are identical to those reported in the literature.⁷ Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{ClO}_3$: C, 57.78; H, 5.73. Found: C, 57.77; H, 5.71.

Isopropyl (3-bromophenyl)(hydroxy)acetate (10): 84% yield. White solid; m.p. 53 - 54 °C; IR (cm^{-1}) 3500 (br), 1733; ^1H NMR δ 1.26 (d, 3H, $J = 6.2$ Hz), 1.32 (d, 3H, $J = 6.2$ Hz), 3.60 (s br, 1H), 5.12 (set, 1H, $J = 6.2$ Hz), 5.17 (s, 1H), 7.19 - 7.52 (m, 4H); ^{13}C NMR δ 21.4, 21.6, 70.6, 72.1, 123.4, 125.0, 129.4, 130.0, 131.3, 132.5, 170.8; exact mass m/z calcd for $\text{C}_{11}\text{H}_{13}\text{BrO}_3$ 272.004806, found 272.004808. Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{BrO}_3$: C, 48.37; H, 4.80. Found: C, 48.36; H, 4.78.

Isopropyl (2-bromophenyl)(hydroxy)acetate (12): 84% yield. White solid; m.p. 52 - 54 °C; IR (cm^{-1}) 3500 (br), 1728; ^1H NMR δ 1.12 (d, 3H, $J = 6.2$ Hz), 1.29 (d, 3H, $J = 6.2$ Hz), 3.49 (s br, 1H), 5.08 (m, 1H, $J = 6.2$ Hz), 5.15 (s, 1H), 7.15 - 7.60 (m, 4H); ^{13}C NMR δ 21.3, 21.5, 70.4, 70.5, 127.7, 128.8, 130.0, 132.2, 133.7, 137.8, 170.5; exact mass m/z calcd for $\text{C}_{11}\text{H}_{13}\text{BrO}_3$ 272.004806, found 272.004809. Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{BrO}_3$: C, 48.37; H, 4.80. Found: C, 48.35; H, 4.77.

Oxidation-Cannizzaro Reaction of Aryl Methyl Ketones. General Procedure.

To a solution of ketone (1.0 mmol) in a 3:1 mixture dioxane/ H_2O (4 mL), SeO_2 (2.0 mmol) and $\text{Yb}(\text{OTf})_3$ (0.1 mmol) were added and the resulting suspension was stirred at 90°C for 18 h. The mixture was filtered through a short pad of Celite[®], the filtrate diluted with 1% aq. NaOH (10 mL) and extracted with CH_2Cl_2 (2 x 10 mL). The aqueous solution was acidified to pH 1 with 10% aq. HCl and extracted with AcOEt (3 x 10 mL). The combined organic phases were dried on Na_2SO_4 , the solvent removed under reduced pressure yielding the desired α -hydroxy aryl acetic acid.

Mandelic acid (13): 90% yield. Identical in all respect to a commercial sample. Anal. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.13; H, 5.29.

(4-Chlorophenyl)(hydroxy)acetic acid (14): 97% yield. White solid; m.p. 152 - 153 °C; IR (cm^{-1}) 3500 (br), 1726; 1H NMR δ 5.08 (s, 1H), 7.23 - 7.55 (m, 4H); ^{13}C NMR δ 72.0, 123.1, 128.0, 128.8, 140.4, 173.6; exact mass m/z calcd for $C_8H_7ClO_3$ 186.008372, found 186.008375. Anal. Calcd. for $C_8H_7ClO_3$: C, 51.50; H, 3.78. Found: C, 51.48; H, 3.76.

(4-Methylphenyl)(hydroxy)acetic acid (15): 84% yield. Yellow solid; m.p. 120 - 122 °C; IR (cm^{-1}) 3500 (br), 1720; 1H NMR δ 5.05 (s, 1H), 7.12 - 7.40 (m, 4H); ^{13}C NMR δ 20.8, 72.5, 127.0, 129.1, 137.3, 137.7, 174.7.; exact mass m/z calcd for $C_9H_{10}O_3$ 166.062994, found 166.062991. Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.06; H, 6.06.

(4-Nitrophenyl)(hydroxy)acetic acid (16): 99% yield. White solid; m.p. 160 - 161 °C; IR (cm^{-1}) 3500 (br), 1725; 1H NMR δ 5.27 (s, 1H), 5.11 (s, 1H), 7.67 - 7.28 (m, 4H); ^{13}C NMR δ 71.9, 123.6, 128.0, 136.7, 148.4, 173.5.; exact mass m/z calcd for $C_8H_7NO_5$ 197.032422, found 197.032420. Anal. Calcd. for $C_8H_7NO_5$: C, 48.74; H, 3.58. Found: C, 48.76; H, 3.56.

(3-Bromophenyl)(hydroxy)acetic acid (17): 78% yield. White solid; m.p. 175 - 177 °C; IR (cm^{-1}) 3500 (br), 1722; 1H NMR δ 5.12 (s, 1H), 7.27 - 7.68 (m, 4H); ^{13}C NMR δ 72.2, 121.8, 126.1, 129.7, 130.7, 130.8, 143.5, 172.5; exact mass m/z calcd for $C_8H_7BrO_3$ 229.957855, found 229.957851. Anal. Calcd. for $C_8H_7BrO_3$: C, 41.59; H, 3.05. Found: C, 41.57; H, 3.06.

(2-Bromophenyl)(hydroxy)acetic acid (18): 78% yield. White solid; m.p. 179 - 180 °C; IR (cm^{-1}) 3500 (br), 1725; 1H NMR δ 5.35 (s, 1H), 7.26 - 7.64 (m, 4H); ^{13}C NMR δ 72.0, 123.2, 128.1, 129.1, 130.2, 132.9, 140.0, 173.5; exact mass m/z calcd for $C_8H_7BrO_3$ 229.957855, found 229.957851. Anal. Calcd. for $C_8H_7BrO_3$: C, 41.59; H, 3.05. Found: C, 41.58; H, 3.07.

Hydroxy(2-naphthyl)acetic acid (19): 99% yield. White solid; m.p. 125 - 126 °C; IR (cm^{-1}) 3500 (br), 1721; 1H NMR δ 5.27 (s, 1H), 7.46 - 8.05 (m, 7H); ^{13}C NMR δ 72.9, 125.3, 125.8, 126.5, 126.7, 128.0, 128.2, 128.3, 133.0, 138.2, 174.5; exact mass m/z calcd for $C_{12}H_{10}O_3$ 202.062994, found 202.062990. Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.27; H, 4.99.

Hydroxy(thien-3-yl)acetic acid (20): 85% yield. White solid; m.p. 145 - 147 °C; IR (cm^{-1}) 3500 (br), 1727; 1H NMR δ 5.22 (s, 1H), 7.43 - 7.77 (m, 3H); ^{13}C NMR δ 72.5, 122.4, 123.8,

126.9, 132.7, 174.2; exact mass m/z calcd for $C_6H_7O_3S$ 159.011591, found 159.011588. Anal.
Calcd. for $C_6H_7O_3S$: C, 45.56; H, 3.82. Found: C, 45.55; H, 3.84.