Supporting Information

Metal-Free, Catalytic Regioselective Oxidative Conversion of Vinylarenes: A Mild Approach to Phenylacetic Acid Derivatives

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1. **Experimental section**

i) **General Information**

All chemicals (reagent grade) were purchased from Sigma-Aldrich and used as received without further purification. $^1$H NMR spectra were recorded at 300 or 500 MHz and $^{13}$C NMR spectra at 75 or 125 MHz in CDCl$_3$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for $^1$H NMR and CDCl$_3$ for $^{13}$C NMR spectra. Coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), brs (broad singlet), d (doublet), dd (doublet of doublet), m (multiplet). TLC inspections were performed on Silica gel 60 F$^{254}$ plates. Column chromatography was performed on silica gel (100-200 mesh) using n-hexane-EtOAc as eluent.

ii) **Typical procedure for the oxidative conversion of styrene (1a) to phenyl acetic acid (2a)**

To a oven dried doubled necked round bottom flask charged with 4 mL of 1,2-dimethoxy ethane (DME) and 1 mL of water was added I$_2$ (0.025 g; 10 mol%) and styrene (1a) (0.104 g, 0.114 mL; 1 mmol). The mixture was stirred for 1 min and the oxone (1.229 g; 2 mmol) was slowly added and continued the stirring at room temperature. The reaction was stopped after 6 h (after completion of the reaction indicated by TLC). The product mixture was extracted with ethyl acetate (3 x 25 mL) and the combined organic layers treated with 5% aqueous sodium thiosulfate (5 mL) solution. Next, the organic layer was dried over anhydrous Na$_2$SO$_4$. The solvent was removed on vacuo and the residue was purified by column chromatography (on silica gel using n-hexane-ethyl acetate as eluent) to yield 2a in 0.120 g (88%) as colourless solid.

iii) **General procedure for the oxidative conversion of 1b-1s**

All the reactions of the substrates 1b-1s were carried out using the typical procedure used for the oxidative conversion of styrene (1a) to phenyl acetic acid (2a).

iv) **Typical procedure for large-scale experiment (20 mmol scale reaction of styrene (1a))**

To a oven dried doubled necked round bottom flask charged with 40 mL of 1,2-dimethoxy ethane (DME) and 10 mL of water was added I$_2$ (0.507 g; 10 mol%) and styrene (1a) (2.083 g, 2.29 mL; 20 mmol). The mixture was stirred for 1 min and the oxone (24.590 g;
40 mmol) was slowly added and continued the stirring at room temperature. The reaction was stopped after 6 h (after completion of the reaction indicated by TLC). The product mixture was extracted with ethyl acetate (1 x 150 and 2 x 100 mL) and the combined organic layers treated with 5% aqueous sodium thiosulfate (25 mL) solution. Next, the organic layer was dried over anhydrous Na$_2$SO$_4$. The solvent was removed on vacuo and the residue was purified by column chromatography (on silica gel using n-hexane-ethyl acetate as eluent) to yield 2a in 2.258 g (83%) as colourless solid.

v) Typical procedure for large-scale experiment (45 mmol scale reaction of styrene (1a))

To a oven dried doubled necked round bottom flask charged with 80 mL of 1,2-dimethoxy ethane (DME) and 20 mL of water was added I$_2$ (1.142 g; 10 mol%) and styrene (1a) (4.686 g, 5.15 mL; 45 mmol). The mixture was stirred for 1 min and the oxone (55.328 g; 90 mmol) was slowly added and continued the stirring at room temperature. The reaction was stopped after 6 h (after completion of the reaction indicated by TLC). The product mixture was extracted with ethyl acetate (1 x 200 and 2 x 125 mL) and the combined organic layers treated with 5% aqueous sodium thiosulfate (60 mL) solution. Next, the organic layer was dried over anhydrous Na$_2$SO$_4$. The solvent was removed on vacuo and the residue was purified by column chromatography (on silica gel using n-hexane-ethyl acetate as eluent) to yield 2a in 5.202 g (85%) as colourless solid.

vi) Typical procedure for large-scale experiment (100 mmol scale reaction of styrene (1a))

To a oven dried doubled necked round bottom flask charged with 120 mL of 1,2-dimethoxy ethane (DME) and 30 mL of water was added I$_2$ (2.538 g; 10 mol%) and styrene (1a) (10.414 g, 11.45 mL; 100 mmol). The mixture was stirred for 1 min and the oxone (122.952 g; 200 mmol) was slowly added and continued the stirring at room temperature. The reaction was stopped after 6 h (after completion of the reaction indicated by TLC). The product mixture was extracted with ethyl acetate (1 x 250 and 2 x 150 mL) and the combined organic layers treated with 5% aqueous sodium thiosulfate (120 mL) solution. Next, the organic layer was dried over anhydrous Na$_2$SO$_4$. The solvent was removed on vacuo and the residue was purified by column chromatography (on silica gel using n-hexane-ethyl acetate as eluent) to yield 2a in 11.696 g (86%) as colourless solid.
2. Spectroscopic data:

2-Phenylacetic acid (2a)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.24-7.36 (m, 5H), 3.64 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 177.88, 133.18, 129.34, 128.61, 127.33, 41.01.

2-(p-tolyl)Acetic acid (2b)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) =7.12-7.17 (m, 4H), 3.60 (s, 2H), 2.32 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) =178.21, 136.90, 130.15, 129.25, 129.13, 40.58, 21.00.

2,4-Dimethylphenylacetic acid (2c)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 6.96-7.08 (m, 3H), 3.61 (s, 2H), 2.29 (s, 3H), 2.27 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 178.12, 137.25, 136.65, 131.20, 130.16, 128.93, 126.82, 38.44, 20.95, 19.42.

(4-tert-butylphenyl)Acetic acid (2d)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 7.34 (d, $J = 8.24$ Hz, 2H), 7.21 (d, $J = 8.39$ Hz, 2H), 3.59 (s, 2H), 1.30 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) =178.18, 150.08, 130.15, 128.96, 125.50, 40.52, 34.38, 31.24.

2-(4-methoxyphenyl)Acetic acid (2e)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.19 (d, $J = 8.69$ Hz, 2H), 6.86 (d, $J = 8.69$ Hz, 2H), 3.79 (s, 3H), 3.58 (s, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) =177.75, 158.81, 130.37, 125.34, 114.04, 55.23, 40.09.

(2-methoxyphenyl)Acetic acid (2f)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.18-7.29 (m, 2H), 6.88-6.94 (m, 2H), 3.83 (s, 3H), 3.66 (s, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) =176.64, 157.38, 130.96, 128.84, 122.33, 120.61, 110.53, 55.47, 35.75.

2-(4-fluorophenyl)Acetic acid (2g)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 10.54 (brs, 1H), 7.23 (dd, $J = 5.47$, 8.68 Hz, 2H), 7.00 (t, $J = 8.68$ Hz, 2H), 3.60 (s, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) =177.47, 163.09, 130.90, 128.86, 115.42, 40.10.

2-(4-chlorophenyl)Acetic acid (2h)
**H NMR (400 MHz, CDCl₃):** δ (ppm) = 7.30 (d, J = 8.43 Hz, 2H), 7.21 (d, J = 8.55 Hz, 2H), 3.61 (s, 2H).

**13C NMR (100 MHz, CDCl₃):** δ (ppm) = 177.33, 133.35, 131.55, 130.71, 128.76, 40.27.

**2-(4-bromophenyl)Acetic acid (2i)**

**H NMR (500 MHz, CDCl₃):** δ (ppm) = 7.46 (d, J = 8.39 Hz, 2H), 7.16 (d, J = 8.39 Hz, 2H), 3.60 (s, 2H).

**13C NMR (125 MHz, CDCl₃):** δ (ppm) = 177.07, 132.11, 131.71, 131.06, 121.43, 40.34.

**2-(3-bromophenyl)Acetic acid (2j)**

**H NMR (500 MHz, CDCl₃):** δ (ppm) = 10.95 (brs, 1H), 7.40-7.44 (m, 2H), 7.18-7.20 (m, 2H), 3.61 (s, 2H).

**13C NMR (125 MHz, CDCl₃):** δ (ppm) = 176.41, 148.28, 135.64, 135.00, 129.52, 124.45, 122.48, 40.33.

**3-Nitrophenylacetic acid (2k)**

**H NMR (500 MHz, CDCl₃):** δ (ppm) = 8.16-8.20 (m, 2H), 7.64-7.66 (m, 1H), 7.52-7.56 (m, 1H), 3.81 (s, 2H).

**13C NMR (125 MHz, CDCl₃):** δ (ppm) = 176.41, 148.28, 135.64, 135.00, 129.52, 124.45, 122.48, 40.33.

**1-Phenyl-2-propanone (2m)**

**H NMR (500 MHz, CDCl₃):** δ (ppm) = 7.31-7.34 (m, 2H), 7.25-7.28 (m, 1H), 7.19-7.21 (m, 2H), 3.69 (s, 2H), 2.14 (s, 3H).

**13C NMR (125 MHz, CDCl₃):** δ (ppm) = 206.31, 134.14, 129.29, 128.64, 126.95, 50.91, 29.16.

**1-(4-chlorophenyl)-2-Propanone (2n)**

**H NMR (500 MHz, CDCl₃):** δ (ppm) = 7.31 (d, J = 8.39 Hz, 2H), 7.13 (d, J = 8.54 Hz, 2H), 3.67 (s, 2H), 2.17 (s, 3H).

**13C NMR (125 MHz, CDCl₃):** δ (ppm) = 205.56, 132.89, 132.51, 130.69, 128.74, 49.93, 29.32.

**2-Phenylpropionic acid (2o)**

**H NMR (500 MHz, CDCl₃):** δ (ppm) = 7.25-7.33 (m, 5H), 3.74 (q, J = 7.17 Hz, 1H), 1.51 (d, J = 7.17 Hz, 3H).

**13C NMR (125 MHz, CDCl₃):** δ (ppm) = 180.09, 139.78, 128.63, 127.56, 127.33, 45.29, 18.11.

**Cyclohexane-1,2-diol (2p)**

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S5
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 4.54-4.60 (m, 1H), 3.53-3.58 (m, 1H), 2.00-2.10 (m, 2H), 1.69-1.74 (m, 2H), 1.25-1.37 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) = 75.81, 32.80, 24.29.

1-Methyl-cyclohexane-1,2-diol (2q)$^{14}$

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 3.47-3.51 (m, 1H), 3.16 (brs, 2H), 1.84 (brs, 1H), 1.57-1.77 (m, 3H), 1.25-1.42 (m, 4H), 1.18 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) = 77.16, 74.13, 38.58, 31.02, 24.08, 23.20, 19.38.

Octane-1,2-diol (2r)$^{15}$

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 3.74–3.63 (m, 2H), 3.43 (dd, $J = 18.82, 7.70$ Hz, 1H), 2.48 (brs, 2H), 1.48–1.23 (m, 10H), 0.88 (t, $J = 6.60$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) = 72.33, 66.78, 33.13, 31.72, 29.28, 25.48, 22.56, 14.03.

Octane-2,3-diol (2s)$^{16a,b}$

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 3.75-3.85 (m, 1H), 3.60-3.65 (m, 1H), 2.06 (s, 2H), 1.26–1.50 (m, 8H), 1.14 (d, $J = 6.60$ Hz, 3H), 0.89 (t, $J = 6.60$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) = 74.90, 70.40, 31.83, 31.70, 25.67, 22.55, 16.45, 13.99.
Copies of $^1$H and $^{13}$C NMR spectra:
Notes and references


