[4-Iodo-3-(isopropylcarbamoyl)phenoxy]acetic Acid as a Highly Reactive and Easily Separable Catalyst for the Oxidative Cleavage of Tetrahydrofuran-2-methanols to γ-Lactones

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1. General experimental
Melting points were determined using a Yanaco micro melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded using a JASCO FT/IR-460Plus spectrometer. All NMR spectra were recorded using JEOL JNM-ECX-400P or JEOL JNM-ECA-500II spectrometers. Proton (¹H) NMR spectra were recorded at 400 or 500 MHz. Carbon-13 (¹³C) NMR spectra were recorded using the broadband proton decoupling at 100 or 126 MHz. All chemical shifts, δ, are stated in units of parts per million (ppm), relative to a standard. For ¹H NMR, the reference point is tetramethylsilane (= 0.00 ppm) or DMSO-d₆ (= 2.49 ppm). For ¹³C NMR, the reference point is CDCl₃ (= 77.0 ppm) or DMSO-d₆ (= 39.7 ppm). High resolution fast atom bombardment (FAB) mass spectra were recorded using a JEOL JMS-AX505 spectrometer. Values are reported as a ratio of mass to charge (m/z). Column chromatography was performed on Nacalai Tesque Silica Gel 60 PF₂₅₄ (0.005–0.050 mm), Kanto Chemical silica gel 60N (0.040–0.050 mm) or Merck 9385 silica gel 60 (0.040–0.063 mm). Thin layer chromatography was performed on Merck 5715 silica gel 60 F₂₅₄ or Merck 5554 silica gel 60 F₂₅₄.
2. Experimental details and analytical data
Methyl [4-iodo-3-(isopropylcarbamoyl)phenoxy]acetate (8)

A solution of 5-hydroxy-2-iodobenzoic acid† (7) (1.17 g, 4.43 mmol) and anhydrous DMF (10 drops) in thionyl chloride (5.5 mL) were heated at reflux with stirring for 3 h under a nitrogen atmosphere. The resulting mixture was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with toluene and the residue was dissolved in anhydrous CH₂Cl₂ (27.5 mL). Isopropylamine (1.90 mL, 22.2 mmol), triethylamine (6.20 mL, 44.3 mmol), and 4-dimethylaminopyridine (82 mg, 0.67 mmol) were added to the solution at 0 °C under a nitrogen atmosphere. After heating under reflux with stirring for 2 h, isopropylamine (0.95 mL, 11.1 mmol) was added to the mixture. The resulting mixture was heated at reflux with stirring for 11 h and then concentrated under reduced pressure. The residue was dissolved in EtOAc and washed with 10% HCl, sat. aq NaHCO₃, water, and brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in anhydrous DMF (25 mL). Methyl bromoacetate (0.42 mL, 4.40 mmol) and K₂CO₃ (1.66 g, 12.0 mmol) were added to the mixture. After heating under reflux with stirring for 3 h, 2H, 3H) 1H NMR (CDCl₃) δ 7.71 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 2.9 Hz, 1H), 6.68 (dd, J = 8.6, 2.9 Hz, 1H), 5.61 (br d, J = 7.5 Hz, 1H), 4.63 (s, 2H), 4.33–4.23 (m, 1H), 3.80 (s, 3H), 1.28 (d, J = 6.3 Hz, 6H); 13C NMR (CDCl₃) δ 168.7, 167.9, 157.9, 143.4, 140.6, 117.8, 114.9, 82.2, 65.2, 52.4, 42.3, 22.6; HRMS (FAB) calcd for C₁₃H₁₁INO₄ ([M+H]+): 378.0202; found 378.0203.

5-(Benzoyloxymethyl)dihydro-2(3H)-furanone (3a)

Oxidative cleavage reaction of 2a (1.06 g, 4.5 mmol) according to the typical procedure gave 3a (874 mg, 88%) as a colorless oil. 1H NMR (CDCl₃) δ 8.05–8.02 (m, 2H), 7.61–7.57 (m, 1H), 7.48–7.44 (m, 2H), 4.91–4.85 (m, 1H), 4.55 (dd, J = 12.2, 3.1 Hz, 1H), 4.46 (dd, J = 12.2, 5.5 Hz, 1H), 2.71–2.55 (m, 2H), 2.48–2.39 (m, 1H), 2.19–2.09 (m, 1H). 13C NMR (CDCl₃) δ 176.5, 166.1, 133.4, 129.7, 129.3, 128.5, 77.4, 65.7, 28.2, 24.0. The data were in accordance with the literature values.²

5-(Acetoxymethyl)dihydro-2(3H)-furanone (3b)

Oxidative cleavage reaction of 2b (70 mg, 0.40 mmol) according to the typical procedure gave 3b (52 mg, 82%) as a colorless oil. 1H NMR (CDCl₃) δ 4.77–4.71 (m, 1H), 4.32 (dd, J = 12.4, 3.2 Hz, 1H), 4.15 (dd, J = 12.4, 5.5 Hz, 1H), 2.66–2.51 (m, 2H), 2.41–2.32 (m, 1H), 2.11 (s, 3H), 2.09–2.00 (m, 1H). 13C NMR (CDCl₃) δ 176.4, 170.5, 77.2, 65.3,
28.1, 23.9, 20.7. The data were in accordance with the literature values.²

2-[(5-Oxotetrahydrofuran-2-ylicyl)isoindoline-1,3-dione (3c)

Oxidative cleavage reaction of 2c (105 mg, 0.40 mmol) according to the typical procedure gave 3c (90 mg, 91%) as a white solid: mp 165–167 °C (hexane/CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.90–7.85 (m, 2H), 7.77–7.73 (m, 2H), 4.91–4.84 (m, 1H), 4.02 (dd, J = 14.0, 7.9 Hz, 1H), 3.84 (dd, J = 14.0, 5.5 Hz, 1H), 2.68–2.51 (m, 2H), 2.44–2.35 (m, 1H), 2.11–2.02 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 176.0, 167.9, 134.2, 131.8, 123.5, 76.6, 41.3, 27.9, 25.4. The data were in accordance with the literature values.²

5-(Tosyloxymethyl)dihydro-2(3H)-furanone (3d)

Oxidative cleavage reaction of 2d (115 mg, 0.40 mmol) according to the typical procedure gave 3d (96 mg, 89%) as a white solid: mp 79–81 °C (hexane/CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.80–7.77 (m, 2H), 7.37 (d, J = 7.8 Hz, 2H), 4.72–4.66 (m, 1H), 4.19 (dd, J = 11.0, 3.7 Hz, 1H), 4.14 (dd, J = 11.0, 4.6 Hz, 1H), 2.64–2.46 (m, 2H), 2.46 (s, 3H), 2.35 (dddd, J = 12.8, 9.6, 7.8, 6.4 Hz, 1H), 2.13 (dddd, J = 12.8, 10.1, 7.3, 6.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.0, 145.4, 132.2, 130.0, 127.9, 76.4, 69.9, 27.8, 23.5, 21.7. The data were in accordance with the literature values.²

5-(Benzyloxymethyl)dihydro-2(3H)-furanone (3e)

Oxidative cleavage reaction of 2e (89 mg, 0.40 mmol) with 4 (7.3 mg, 0.02 mmol), Oxone® (984 mg, 1.6 mmol), and BHT (9, 88 mg, 0.4 mmol) in a 10:1 mixture of MeNO₂ and DMF (1.8 mL) at 50 °C gave 3e (68 mg, 83%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.27 (m, 5H), 4.70–4.65 (m, 1H), 4.59 (dd, J = 11.9 Hz, 1H), 4.56 (d, J = 11.9 Hz, 1H), 3.68 (dd, J = 10.5, 3.2 Hz, 1H), 3.59 (dd, J = 10.5, 4.1 Hz, 1H), 2.63 (dd, J = 17.9, 10.1, 6.4 Hz, 1H), 2.49 (dd, J = 17.9, 10.1, 6.9 Hz, 1H), 2.34–2.25 (m, 1H), 2.18–2.09 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 177.3, 137.6, 128.5, 127.8, 127.6, 79.0, 73.6, 71.5, 28.4, 24.1. The data were in accordance with the literature values.²

Dihydro-5-tetradecyl-2(3H)-furanone (3f)

Oxidative cleavage reaction of 2f (119 mg, 0.40 mmol) according to the typical procedure gave 3f (97 mg, 86%) as a white solid: mp 40–43 °C (hexane); ¹H NMR (400 MHz, CDCl₃) δ 4.52–4.45 (m, 1H), 2.55–2.51 (m, 2H), 2.36–2.28 (m, 1H), 1.90–1.80 (m, 1H), 1.77–1.70 (m, 1H), 1.63–1.55 (m, 1H), 1.49–1.26 (m, 24H), 0.88 (t, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.3, 81.0, 35.6, 31.9, 29.7, 29.62, 29.59, 29.50, 29.4, 29.33, 29.32, 28.8, 28.0, 25.2, 22.7, 14.1. The data were in accordance with the literature values.²
Ethyl 4-(5-oxotetrahydrofuran-2-yl)butanoate (3g)

Oxidative cleavage reaction of 2g (87 mg, 0.40 mmol) according to the typical procedure gave 3g (60 mg, 75%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.53–4.46 (m, 1H), 4.14 (q, $J = 7.3$ Hz, 2H), 2.55 (d, $J = 9.6$ Hz, 1H), 2.53 (dd, $J = 9.6$, 0.9 Hz, 1H), 2.39–2.30 (m, 3H), 1.92–1.65 (m, 5H), 1.26 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.0, 173.1, 80.4, 60.4, 34.8, 33.7, 28.7, 27.9, 20.8, 14.2. The data were in accordance with the literature values.²

Dihydro-4-phenyl-2(3H)-furanone (3h)

Oxidative cleavage reaction of 2h (71 mg, 0.40 mmol) according to the typical procedure gave 3h (55 mg, 85%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40–7.35 (m, 2H), 7.33–7.28 (m, 1H), 7.25–7.22 (m, 2H), 4.67 (dd, $J = 9.2$, 7.9 Hz, 1H), 4.27 (dd, $J = 9.2$, 7.9 Hz, 1H), 3.84–3.75 (m, 1H), 2.93 (dd, $J = 17.7$, 9.2 Hz, 1H), 2.68 (dd, $J = 17.7$, 9.2 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 176.4, 139.4, 129.1, 127.7, 126.7, 74.0, 41.1, 35.7. The data were in accordance with the literature values.²

4-(Benzylxoymethyl)dihydro-2(3H)-furanone (3i)

Oxidative cleavage reaction of 2i (89 mg, 0.40 mmol) with 4 (7.3 mg, 0.02 mmol), Oxone® (984 mg, 1.6 mmol), and BHT (9, 88 mg, 0.4 mmol) in a 10:1 mixture of MeNO$_2$ and DMF (1.8 mL) at 50 °C gave 3i (68 mg, 83%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38–7.28 (m, 5H), 4.52 (s, 2H), 4.40 (dd, $J = 9.2$, 7.8 Hz, 1H), 4.18 (dd, $J = 9.2$, 5.5 Hz, 1H), 3.49 (dd, $J = 9.2$, 5.5 Hz, 1H), 3.46 (dd, $J = 9.2$, 6.4 Hz, 1H), 2.89–2.79 (m, 1H), 2.60 (dd, $J = 17.9$, 9.2 Hz, 1H), 2.37 (dd, $J = 17.9$, 6.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.8, 137.5, 128.5, 127.9, 127.6, 73.3, 70.7, 70.3, 35.4, 31.1. The data were in accordance with the literature values.²

5-(Benzylxoymethyl)dihydro-5-methyl-2(3H)-furanone (3j)

Oxidative cleavage reaction of 2j (100 mg, 0.40 mmol) according to the typical procedure gave 3j (86 mg, 92%) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.03–8.00 (m, 2H), 7.61–7.58 (m, 1H), 7.48–7.44 (m, 2H), 4.41 (d, $J = 11.5$ Hz, 1H), 4.36 (d, $J = 11.5$ Hz, 1H), 2.73 (dd, $J = 18.3$, 10.3, 8.0 Hz, 1H), 2.67 (dd, $J = 18.3$, 10.3, 5.7 Hz, 1H), 2.35 (dd, $J = 13.2$, 10.3, 5.7 Hz, 1H), 2.10 (dd, $J = 13.2$, 10.3, 8.0 Hz, 1H), 1.54 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 176.2, 166.0, 133.4, 129.6, 129.3, 128.6, 84.0, 69.3, 30.4, 29.2, 23.8. The data were in accordance with the literature values.²
3. $^1$H and $^{13}$C NMR Spectra

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
\(^1\text{H NMR (500 MHz, DMSO-}d_6\text{)}\)

\(^{13}\text{C NMR (126 MHz, DMSO-}d_6\text{)}\)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
\(^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\)

\(^{13}\text{C} \text{NMR (126 MHz, CDCl}_3\text{)}\)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
4. References
