Supporting Information for:

Iodination of Organic Substrates with Halide Salts and H_2O_2 Using an Organotelluride Catalyst

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General Methods. Solvents and reagents were used as received from Sigma-Aldrich Chemical Co (St. Louis, MO) unless otherwise noted. Concentration *in vacuo* was performed on a Büchi rotary evaporator. NMR spectra were recorded at 30.0 ˚C on a Varian Gemini-300, Inova 400, or Inova 500 instruments with residual solvent signal as internal standard: $CDCl_3$ (δ 7.26 for proton, δ 77.0 for carbon). Infrared spectra were recorded on a Perkin-Elmer FT-IR instrument. UV-visible-near-IR spectra were recorded on a Perkin-Elmer Lambda 12 spectrophotometer or on a Sequential SX.18MV Stopped-Flow Spectrometer (Applied Photophysics, Leatherhead, UK). Both were equipped with a circulating constant-temperature bath for the sample chambers. Elemental analyses were conducted by Atlantic Microanalytical, Inc.

Preparation of Bis-1-[4-*N*,*N*-bis(carboethoxymethyl)aminophenyl Ditelluride (3). 4-*N*,*N*-Bis(carboethoxymethyl)aniline (5.30 g, 0.020 mol) in 50 mL of EtOAc was added dropwise to a stirred slurry of $TeCl_4$ (5.39 g, 0.020 mol) and pyridine (1.60 g, 0,20 mol) in 50 mL of EtOAc cooled to 0 °C. The reaction was allowed to warm to room temperature following addition and was stirred for 15 h. The solid product was collected by filtration, dried, and stirred with a mixture of 200 mL of toluene and 200 mL of 10% sodium bisulfite. The aqueous layer was extracted with toluene (2 x 100 mL). The combined toluene extracts were dried over $MgSO_4$, filtered through a pad of Celite, and concentrated to give a mixture of the monotelluride (33%) and the ditelluride 3 (67%) in 6.34 g (85% combined yield) isolated yield as a red oil: ^{1}H NMR ($CDCl_3$) δ 7.61 (ditelluride, AA'BB', 4 H, *J*("doublet") = 9 Hz), 7.53 (monotelluride, AA'BB', 4 H, *J*("doublet") = 9 Hz), 6.43 (mixture, AA'BB', 4 H, *J*("doublet") = 9 Hz), 4.21 (mixture, q, 8 H, *J* = 7 Hz), 4.12 (s, 8 H), 1.27 (mixture, t, 12 H, *J* = 7 Hz). The product ratio is determined by the ratio of the peaks at δ 7.61 and 7.53; IR (mixture, film, NaCl) 1745 cm^{-1}; FAB(+)MS, *m/z* 789 ($C_{28}H_{36}N_2O_8{}^{130}Te_2 + H^+$), 659 ($C_{28}H_{36}N_2O_8{}^{130}Te + H^+$).

Preparation of 1-[4-*N*,*N*-bis(carboethoxymethyl)aminophenyltelluro]-3-phenoxypropane (4). Sodium borohydride (0.77 g, 20 mmol) was added in small portions over a 1-h period to a solution of bis-4-*N*,*N*-bis(carboethoxymethyl)aminophenyl ditelluride (**3**, 13.92 g, 11.72 mmol from a 2:1 mixture with the monotelluride) in a 1:1 by volume mixture of ethanol and THF. After the dark red color of the ditelluride had faded, 3-phenoxypropyl bromide (4.36 g, 20.3 mmol) was added and the resulting solution was heated at reflux for 15 h. The reaction mixture was concentrated and the residue was partitioned between CH_2Cl_2 and brine. Both

phases were filtered through a pad of Celite® to remove tellurium metal and the aqueous phase was further extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was purified via chromatography on SiO_2 eluted with CH_2Cl_2 to give 7.87 g (74%) of **4** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.62 (AA'BB', 2 H, *J* ("doublet") = 9 Hz), 7.26 (t, 2 H, *J* = 7 Hz), 6.92 (t, 1 H, *J* = 7 Hz), 6.85 (d, 2 H, *J* = 8 Hz), 6.44 (AA'BB', 2 H, *J* ("doublet') = 9 Hz), 4.21 (q, 4 H, *J* = 7 Hz), 4.11 (s, 4 H), 3.97 (t, 4 H, *J* = 7 Hz), 2.90 (t, 2 H, *J* = 7 Hz), 2.19 (quint, 2 H, *J* = 7 Hz), 1.27 (t, 6 H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 170.60, 158.78, 147.82, 141.05, 129.35, 120.56, 114.45, 113.42, 97.19, 68.58, 61.21, 53.26, 31.17, 14.20, 4.40; IR (film, NaCl) 1745 cm^{-1}; FAB(+)MS, *m/z* 529 ($C_{23}H_{29}NO_5{}^{130}$Te). **Anal.** Calcd for $C_{23}H_{29}NO_5Te$: C, 52.41; H, 5.55; N, 2.66. Found: C, 52.64; H, 5.61; N, 2.59.

Preparation of 1-[4-*N*,*N*-bis(carboxalatomethyl)aminophenyltelluro]-3-phenoxypropane Disodium Salt (1). A solution of 10% sodium hydroxide (7.0 mL) was added to a solution of bisester **4** (1.52 g, 2.88 mmol) in 30 mL of EtOH. The resulting mixture was heated at reflux for 1 h and was then cooled to ambient temperature. The crystalline product was collected by filtration, washed with a cold mixture of 2:1 ether/ethanol, and dried. Product yield was 1.45 g (97%) of **1** as a white, crystalline solid (mp > 250 °C with decomposition): ^{1}H NMR (CD_3OD) δ 7.52 (AA'BB', 2 H, *J*("doublet") = 9 Hz), 7.52 (t, 2 h, *J* = 8 Hz), 6.87 (t, 1 H, *J* = 8 Hz), 6.84 (d, 2 H, *J* = 8 Hz), 6.47 (AA'BB', 2 H, *J*("doublet") = 9 Hz), 3.95 (t, 2 H, *J* = 7 Hz), 3.90 (s, 4 H), 3.29 (quint, 2 H, *J* = 7 Hz), 2.81 (t, 2 H, *J* = 7 Hz); IR (KBr) 1592 cm^{-1}. **Anal.** Calcd for $C_{19}H_{19}NNa_2O_5Te$: C, 44.32; H, 3.72; N, 2.72. Found: C, 44.20; H, 3.71; N, 2.77.

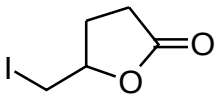
Kinetics Experiments. The rate of oxidation of compound **1** with hydrogen peroxide (0.0018 to 0.040 M) was measured at 298.0 ± 0.2 K in 0.01 M sodium dihydrogenphosphate (pH 6.0). Oxidations were studied under pseudo-first order conditions with an excess of hydrogen peroxide. Decays of the characteristic absorption band of the compound (λ_{max} of 277 nm for **1**) were fit to single-exponential functions using a Curfit subroutine that employed Marquardt algorithms. All runs were replicated 3 to 5 times on the Sequential SX.18MV stopped-flow spectrophotometer. Equal volumes of H_2O_2 in 0.01 M NaH_2PO_4 and telluride **1** in 0.01 M NaH_2PO_4 were combined in the mixing chamber to give final concentrations that were one-half of the starting concentrations. Values of k_{obs} are compiled in Table S1.

For compound **1** (2.5×10^{-4} M final concentration), the final H_2O_2 concentration was varied from 0.0046 to 0.035 M, and a linear dependence originating from (0,0) with the second-order rate constant k of $(3.93 \pm 0.08) \times 10^2$ M^{-1} s^{-1} was observed.

Table S1. Rate of oxidation of **1** at varying H_2O_2 concentration and constant concentration of chalcogenide in pH 6.0 phosphate buffer at 298.0 ± 0.2 K

[**1**], M	[H_2O_2], M	k_{obs}, s^{-1}
2.5×10^{-4}	0.0	$< 10^{-4}$
2.5×10^{-4}	0.46×10^{-2}	1.84 ± 0.03
2.5×10^{-4}	1.0×10^{-2}	3.91 ± 0.03
2.5×10^{-4}	1.7×10^{-2}	6.43 ± 0.08
2.5×10^{-4}	3.5×10^{-2}	13.8 ± 0.1

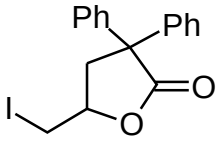
General Procedure for Iodinations: The substrate (2.5 mmol) and catalyst **1** (10.3 mg, 0.020 mmol) were dissolved in a stirred mixture of 25 mL of ether and 50 mL of pH-6 phosphate buffer at ambient temperature. Sodium iodide as a 2 M solution (2.75–5.0 mL) and 2 M H_2O_2 (2.1-6.3 mL) were added independently in small aliquots via syringe every 5 min over a 45-min interval in the stoichiometry described in Table 1. The reaction mixtures were stirred until reaction was complete (1-5 h) as monitored by ^{1}H NMR and thin layer chromatography. The organic phase was separated and the aqueous layer extracted with two additional aliquots of ether. The combined ether extracts were washed with brine and then 3% sodium bisulfite, were dried over $MgSO_4$, and concentrated. The crude product was purified via chromatography on silica gel or recrystallization for crystalline products.



Entry 1. Preparation of 5-Iodo-γ-valerolactone: 4-pentenoic acid (250 mg, 2.5 mmol) was treated with 2.0 M sodium iodide (1.38 mL, 2.75 mmol), 2.0 M hydrogen peroxide (2.1 mL,

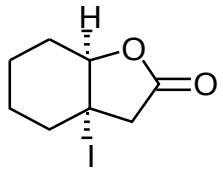
4.2 mmol), and catalyst **1** as described. The reaction was complete in 1 hour at which time it was worked up according to the general procedure to give the product, 5-iodo-γ-valerolactone (531 mg, 94%) as a red oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.48-4.57 (m, 1 H), 3.25-3.41 (m, 2 H), 2.39-2.68 (m, 3 H), 1.90-2.04 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.03, 78.06, 28.50, 27.62, 7.96; IR (NaCl plate, film) 1772 cm^{-1} (C=O). (References for IR, and NMR data: Grossman, R.B., Trupp, R.J. *Can. J. Chem.* **1998**, *76*, 1233-1237. Zhao, Y., Pei, C., Wong, Z., Xi, S. *Phosphorus, Sulfur, and Silicon* **1992**, *66*, 115-125.)

Entry 8. Preparation of 5-Iodo-γ-valerolactone: 4-Pentenoic acid sodium salt (0.305 g, 4.10 mmoles) was treated with 2.0 M sodium iodide (1.38 mL, 2.75 mmole), 2.0 M hydrogen peroxide (2.1 mL, 4.2 mmol), and catalyst **1** as described, except that no organic cosolvent was added. The reaction was complete in 1 hour after which it was worked up according to the general procedure to give the product, 5-iodo-γ-valerolactone (497mg, 88%) as a red oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.48-4.57 (m, 1 H), 3.25-3.41 (m, 2 H), 2.39-2.68 (m, 3 H), 1.90-2.04 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.03, 78.06, 28.50, 27.62, 7.96; IR (NaCl plate, film) 1772 cm^{-1} (C=O). (References for IR, and NMR data: Grossman, R.B., Trupp, R.J. *Can. J. Chem.* **1998**, *76*, 1233-1237. Zhao, Y., Pei, C., Wong, Z., Xi, S. *Phosphorus, Sulfur, and Silicon* **1992**, *66*, 115-125.)

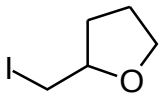


Entry 2. Preparation of (5-Iodomethyl-3,3-diphenyldihydrofuran-2-one): 2,2-diphenyl-4-pentenoic acid (631 mg, 2.5 mmol) was treated with 2.0 M sodium iodide (5.0 mL, 10 mmol), 2.0 M hydrogen peroxide (6.25 mL, 12.5 mmol), and catalyst **1** as described. The reaction was complete after 1 h. The reaction was worked up following the general procedure. Purification was done via column chromatography on silica gel eluting with 1:4 hexanes:DCM to give the product 5-iodomethyl-3,3-diphenyl-dihydro-furan-2-one (876 mg, 93%) as a white solid: mp, 114-116 °C (lit. mp, 116-117 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.36 (m, 10 H), 4.33-4.42 (m, 1 H), 3.39-3.44 (m, 1 H), 3.27-3.3 (m, 1 H), 3.17-3.24 (m, 1 H), 2.62-2.69 (m,

1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.37, 141.56, 139.40, 129.04, 128.52, 127.95, 127.65, 127.45, 127.27, 75.38, 58.67, 44.10, 5.82; IR (KBr) 1763 (C=O). (Reference for mp: Arnold. R.T., Lindsay, K.L. *J. Am. Chem. Soc.* **1953**, *75*, 1048-1049.)

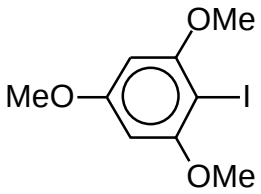


Entry 3. Preparation of 3a-Iodohexahydrobenzofuran-2-one: 2-(1-Cyclohexen-1-yl) acetic acid (350 mg, 2.50 mmol) was treated with 2.0 M sodium iodide (1.38 mL, 2.75 mmol), 2.0 M hydrogen peroxide 2.1 mL, 4.2 mmol), and catalyst **1** as described. After 5 h, the reaction was worked up as described. The crude product was redissolved in DCM and extracted with saturated $NaHCO_3$ (aqueous), dried over magnesium sulfate and concentrated. Purification was done by column chromatography on silica gel eluting with DCM to give the product 3a-iodohexahydrobenzofuran-2-one (266 mg, 40%) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.77 (t, 1 H, J = 3.6 Hz), 3.04 (dd, 2 H, J = 16.8 Hz), 2.00-2.18 (m, 4 H), 1.46-1.69 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.23, 86.20, 50.23, 39.40, 36.73, 24.28, 22.09, 19.20; IR (NaCl plate, film) 1788 cm^{-1} (C=O). (References: Motohashi, S., Satomi, M., Fujimoto, Y., Tatsuno, T*Heterocycles* **1985**, *23*, 2035-2039. Klein. J. *J. Am. Chem. Soc.* **1959**, *81*, 3611-3614.)

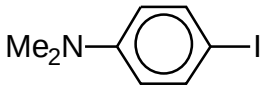


Entry 4. Preparation of 2-Iodomethyltetrahydrofuran: 4-Penten-1-ol (215 mg, 2.5 mmol) was treated with 2.0 M sodium iodide (2.75 mL, 5.5 mmol), 2.0 M hydrogen peroxide (4.25 mL, 8.5 mmol), and catalyst **1** as described. After 5 h, the reaction was worked up as described. Purification was done by column chromatography on silica gel eluting with 1:4 EtOAc:hexanes to give 2-(iodomethyl)tetrahydrofuran (308 mg, 58%) as a brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84-3.95 (m, 2 H), 3.71-3.78 (m, 1 H), 3.10-3.20 (m, 2 H), 1.77-2.09 (m, 3 H), 1.53-1.64 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 78.27, 68.74, 31.72, 25.94, 10.38.

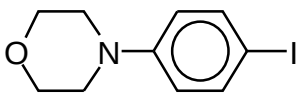
(Reference for NMR data: Hoffmann, R.W., Koberstein, R., Harms, K. *J. Chem. Soc., Perkin Trans. 2* **1999**, 183-191.)



Entry 5. Preparation of 2-Iodo-1,3,5-trimethoxybenzene: 1,3,5-trimethoxybenzene (420 mg, 2.50 mmol) was treated with 2.0 M sodium iodide (4.50 mL, 9.0 mmol), 2.0 M hydrogen (5.0 mL, 10.0 mmol), and catalyst **1** as described. After 3 h, the reaction was worked up as described in the general procedure. Chromatography on silica gel eluted with CH_2Cl_2 gave 2-iodo-1,3,5-trimethoxybenzene (691 mg, 94%): mp 117-120 °C (lit. mp, 120 °C) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (s, 2 H), 3.85 (s, 6 H), 3.81 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.03 159.63, 91.07, 66.50, 56.33, 55.41. (Reference for mp: Vasil'ev, A.A., Engman, L. *J. Org. Chem.* **1998**, *63*, 3911-3917.)



Entry 6. Preparation of 4-Iodo-*N,N*-dimethylaniline: N,N-Dimethylaniline (303 mg, 2.50 mmol) was treated with 2.0 M sodium iodide (4.50 mL g, 9.0 mmol), 2.0 M hydrogen peroxide (6.3 ml, 12.5 mmol), and catalyst **1** as described. After 5 h, the reaction was worked up as described in the general procedure. Chromatography on silica gel eluted with CH_2Cl_2 gave 4-iodo-*N,N*-dimethylaniline (543 mg, 88%) as a white solid: mp 72-74 °C (lit mp, 66-67 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (AA'BB', 2 H, J ("doublet") = 9 Hz), 6.49 (AA'BB', 2 H, J ("doublet") = 9 Hz), 2.92 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.81, 137.39, 114.58, 77.30, 40.26. (Reference for NMR and mp: Bachki, A., Foubelo, F., Yus, M. *Tetrahedron* **1994**, *50*, 5139-5146.)



Entry 7. *N*-(4-iodophenyl)morpholine: *N*-Phenylmorpholine (408 mg, 2.5 mmol)) was treated with 2.0 M sodium iodide (5.0 mL, 10.0 mmol), 2.0 M hydrogen peroxide (6.3 mL, 12.5 mmol), and catalyst **1** as described. After 5 h, the reaction was worked up as described in the general procedure. Chromatography on silica gel eluted with CH_2Cl_2 gave *N*-(4-iodophenyl)morpholine, which was recrystallized from ethanol to give 553 mg (76%) of a white solid: mp 146-149 °C (lit. mp, 146 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (AA'BB', 2 H, J ("doublet") = 9 Hz), 6.66 (AA'BB', 2 H, J ("doublet") = 9 Hz), 3.84 (t, 4 H, J = 5 Hz), 3.11 (t, 4 H, J = 5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.88, 137.85, 117.69, 81.78, 66.70, 48.88. (Reference for mp: Effenberger, F., Agster, W., Fischer, P., Jogun, K.H., Stezowski, J.J., Daltrozzo, E., Kollmannsberger-von Nell, G. *J. Org Chem.* **1983**, *48*, 4649-4658.)