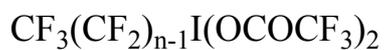


SUPPORTING INFORMATION FOR

An Easily Accessed Class of Recyclable Hypervalent Iodide Reagents for Functional
Group Oxidations: bis(trifluoroacetate) Adducts of Fluorous Alkyl Iodides,



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General Data. Chemicals were treated as follows: methanol and CHCl_3 , distilled; FC-72, $\text{CF}_3\text{C}_6\text{F}_{11}$, R_{f7}I , R_{f8}I , R_{f10}I , R_{f12}I ($6 \times \text{ABCR}$), trifluoroacetic anhydride (Lancaster or Acros), acetone- d_6 , methanol- d_4 ($2 \times \text{Aldrich}$), 1,4-hydroquinone, 2,3,5-trimethyl-1,4-hydroquinone, 2,6-di(*t*-butyl)-1,4-hydroquinone, and 2,5-dichloro-1,4-hydroquinone ($4 \times \text{Acros}$), used as received. The ~80% H_2O_2 was prepared from 30% H_2O_2 by reducing the volume 1/2.7 in vacuo at 50 °C,^{s1} and standardized by titration with KMnO_4 .^{s2}

NMR spectra were recorded on standard Bruker 400 or 300 MHz FT spectrometers at ambient temperatures and referenced as follows: ^1H , residual internal acetone- d_5 (δ 2.04) or methanol- d_3 (δ 3.30); ^{13}C , internal acetone- d_6 (δ 29.8) or methanol- d_4 (δ 49.0); ^{19}F , internal C_6F_6 (δ -162.0). IR spectra were measured on an ASI React-IR spectrometer. Elemental analyses were conducted with a Carlo Erba EA1110 instrument.

$\text{R}_{f7}\text{I}(\text{OCOCF}_3)_2$ (2- R_{f7}). A round bottom flask was charged with ~80% H_2O_2 (0.25 mL, 8.00 mmol)^{s1} and cooled to -10 °C. Then trifluoroacetic anhydride (1.65 mL, 14.9 mmol) was added with stirring. The cold bath was removed. After 30 min, the mixture was cooled to -15 °C, and 1- R_{f7} (0.45 mL, 0.91 g, 1.83 mmol) was added with stirring. The mixture was stirred for 3 h at 0 °C, and then allowed to stand for 48 h at 20 °C. The volatiles were removed by oil pump vacuum (-78 °C trap), and the residue collected to give 2- R_{f7} as a white solid (1.190 g, 1.648 mmol, 97%), m.p. 110.0-111.5 °C dec. Calcd for $\text{C}_{11}\text{F}_{21}\text{IO}_4$: C, 18.28. Found: C, 17.58.

MS (FAB^+ , m/Z): 609 ($\text{M}^+ - \text{OCOCF}_3$, 30%), 1330 ($2\text{M}^+ - \text{OCOCF}_3$,^{s3} 100%). IR (cm^{-1} , thin film): ν_{CO} 1739 (ms), 1686 (ms); ν_{CF} 1212-1069 (vs).

NMR (δ , acetone- d_6): $^{13}\text{C}\{^1\text{H}\}$ 114.1 (q, $^1J_{\text{CF}} = 287.5$ Hz, CF_3CO), 160.9 (q, $^2J_{\text{CF}} = 41.2$ Hz, CF_3CO); ^{19}F -73.67 (s, 6F, CF_3CO), -77.79 (t, $^4J_{\text{FF}} = 15.1$ Hz,^{s4} 2F, CF_2I), -78.97 (t, $^4J_{\text{FF}} = 10.0$ Hz,^{s4} 3F, CF_3CF_2), -113.42 (m, 2F, CF_2), -119.31 (m, 2F, CF_2), -119.66 (m, 2F, CF_2), -120.55 (m, 2F, CF_2), -124.05 (m, 2F, CF_2).

$\text{R}_{f8}\text{I}(\text{OCOCF}_3)_2$ (2- R_{f8}). A round bottom flask was charged with ~80% H_2O_2 (0.25 mL, 8.00 mmol)^{s1} and cooled to -10 °C. Then trifluoroacetic anhydride (1.65 mL, 14.9 mmol) was added dropwise with stirring. The cold bath was removed. After 30 min, the mixture was cooled to -15 °C, and 1- R_{f8} (0.50 mL, 1.00 g, 1.83 mmol) was added with stirring. The mixture was stirred for 3 h at 0 °C, and then allowed to stand for 48 h at 20 °C. The volatiles were removed by oil pump

vacuum ($-78\text{ }^{\circ}\text{C}$ trap), and the residue collected to give **2-R_{f8}** as a white solid (1.385 g, 1.795 mmol, 98%), m.p. 112.0-113.5 $^{\circ}\text{C}$ dec. Calcd for $\text{C}_{12}\text{F}_{23}\text{IO}_4$: C, 18.65. Found: C, 18.38.

MS (FAB⁺, *m/z*): 659 ($\text{M}^+ - \text{OCOCF}_3$,^{s3} 50%), 1431 ($2\text{M}^+ - \text{OCOCF}_3$, 100%). IR (cm^{-1} , thin film): ν_{CO} 1741 (ms), 1687 (ms); ν_{CF} 1216-1096 (vs).

NMR (δ , acetone- d_6): $^{13}\text{C}\{^1\text{H}\}$ 114.1 (q, $^1J_{\text{CF}} = 287.3$ Hz, CF_3CO), 160.9 (q, $^2J_{\text{CF}} = 41.2$ Hz, CF_3CO); ^{19}F -73.73 (s, 6F, CF_3CO), -78.10 (t, $^4J_{\text{FF}} = 14.0$ Hz,^{s4} 2F, CF_2I), -79.02 (t, $^4J_{\text{FF}} = 10.2$ Hz,^{s4} 3F, CF_3CF_2), -113.44 (m, 2F, CF_2), -119.36 (m, 4F, CF_2), -119.71 (m, 2F, CF_2), -120.55 (m, 2F, CF_2), -124.09 (m, 2F, CF_2).

R_{f10}I(OCOCF₃)₂ (2-R_{f10}). A round bottom flask was charged with $\sim 80\%$ H_2O_2 (1.19 mL, 38.0 mmol)^{s1} and cooled to $-10\text{ }^{\circ}\text{C}$.^{s5} Then trifluoroacetic anhydride (7.00 mL, 63.2 mmol) was added dropwise with stirring. The cold bath was removed. After 30 min, the mixture was cooled to $-15\text{ }^{\circ}\text{C}$, and **1-R_{f10}** (1.182 g, 1.830 mmol) was added with stirring. The mixture was stirred for 3 h at $0\text{ }^{\circ}\text{C}$, and then allowed to stand for 48 h at $20\text{ }^{\circ}\text{C}$. The volatiles were removed by oil pump vacuum ($-78\text{ }^{\circ}\text{C}$ trap), and the residue collected to give **2-R_{f10}** as a white solid (1.413 g, 1.620 mmol, 89%), m.p. 115.0-116.5 $^{\circ}\text{C}$ dec. Calcd for $\text{C}_{14}\text{F}_{27}\text{IO}_4$: C, 19.27. Found: C, 18.49.

MS (FAB⁺, *m/z*): 759 ($\text{M}^+ - \text{OCOCF}_3$, 46%), 1631 ($2\text{M}^+ - \text{OCOCF}_3$,^{s3} 100%). IR (cm^{-1} , thin film): ν_{CO} 1745 (ms), 1691 (ms); ν_{CF} 1216-1096 (vs).

NMR (δ , acetone- d_6): $^{13}\text{C}\{^1\text{H}\}$ 114.1 (q, $^1J_{\text{CF}} = 287.4$ Hz, CF_3CO), 160.9 (q, $^2J_{\text{CF}} = 41.1$ Hz, CF_3CO); ^{19}F -73.71 (s, 6F, CF_3CO), -77.77 (t, $^4J_{\text{FF}} = 13.3$ Hz,^{s4} 2F, CF_2I), -79.04 (t, $^4J_{\text{FF}} = 10.1$ Hz,^{s4} 3F, CF_3CF_2), -113.36 (m, 2F, CF_2), -119.44 (m, 10F, CF_2), -120.54 (m, 2F, CF_2), -124.08 (m, 2F, CF_2).

R_{f12}I(OCOCF₃)₂ (2-R_{f12}). A round bottom flask was charged with $\sim 80\%$ H_2O_2 (1.64 mL, 52.4 mmol)^{s1} and cooled to $-10\text{ }^{\circ}\text{C}$.^{s5} Then trifluoroacetic anhydride (7.89 mL, 73.1 mmol) was added dropwise with stirring. The cold bath was removed. After 30 min, the mixture was cooled to $-15\text{ }^{\circ}\text{C}$, and **1-R_{f12}** (1.365 g, 1.829 mmol) was added with stirring. The mixture was stirred for 3 h at $0\text{ }^{\circ}\text{C}$, and was allowed to stand for 48 h at $20\text{ }^{\circ}\text{C}$. The volatiles were removed by oil pump vacuum ($-78\text{ }^{\circ}\text{C}$ trap), and the residue collected to give **2-R_{f12}** as a white solid (1.654 g, 1.701 mmol, 93%), m.p. 121.0-122.5 $^{\circ}\text{C}$ dec. Calcd for $\text{C}_{16}\text{F}_{31}\text{IO}_4$: C, 19.75. Found: C, 19.06.

MS (FAB⁺, *m/z*): 859 (M⁺–OCOCF₃, 80%), 1830 (2M⁺–OCOCF₃,^{s3} 100%). IR (cm⁻¹, thin film): ν_{CO} 1742 (ms), 1688 (ms); ν_{CF} 1194-1094 (vs).

NMR (δ , acetone-d₆): ¹³C{¹H} 114.1 (q, ¹J_{CF} = 287.5 Hz, CF₃CO), 160.9 (q, ²J_{CF} = 41.3 Hz, CF₃CO); ¹⁹F –73.94 (s, 6F, CF₃CO), –77.72 (t, ⁴J_{FF} = 13.2 Hz,^{s4} 2F, CF₂I), –78.97 (t, ⁴J_{FF} = 10.0 Hz,^{s4} 3F, CF₃CF₂), –113.38 (m, 2F, CF₂), –119.42 (m, 14F, CF₂), –120.54 (m, 2F, CF₂), –124.05 (m, 2F, CF₂).

Oxidations of Hydroquinones. A. (Chart 1; Entries 1, 3, 4, 8) A flask was charged with **3a,b,d** (0.9 mmol) and **2-R_{fn}** (0.9 mmol). Then methanol (5 mL) was added with stirring. The mixture immediately turned yellow. After 2-3 h, CF₃C₆F₁₁ (2 mL) was added. The organic and fluoruous phases were stirred and separated. The fluoruous phase was extracted with methanol (2 × 3 mL) and the methanol phase with CF₃C₆F₁₁ (2 × 3 mL). The solvents were removed from combined fluoruous and methanol phases by rotary evaporation to give **4a,b,d** and **1-R_{fn}** as summarized in Table 2. The conversions were assayed by ¹H NMR; spectroscopic data have been previously summarized.^{s6} No other species could be detected.

B. (Chart 1; Entries 2, 5, 6, 7) A 5 mm NMR tube was sequentially charged with **3a-c** (0.09 mmol), methanol-d₄ (0.5 mL; shaken to give a solution), and **2-R_{fn}** (0.09 mmol). The mixture immediately turned yellow. ¹H NMR were immediately recorded, and showed complete conversions.

C. (Chart 2) A flask was charged with **2-R_{f10}** (1.000 g, 1.146 mmol), **3a** (0.1262 g, 1.146 mmol), and methanol (5 mL). The suspension was stirred and turned yellow. After 1 h, FC-72 (5 mL) was added. The two phases were separated. The fluoruous phase was extracted with methanol (2 × 3 mL) and the methanol phase with FC-72 (2 × 3 mL). The methanol phases were combined, and the fluoruous phases were combined. The solvents were removed by rotary evaporation to give green-yellowish **4a** (0.1235 g, 1.142 mmol, >99%) that contained 9% of **3a** by ¹H NMR, and **1-R_{f10}** (0.7359 g, 1.139 mmol, 99%).

A flask was similarly charged with **2-R_{f10}** (0.7022 g, 0.8053 mmol; prepared from the **1-R_{f10}** from the previous cycle; 71% yield),^{s1} **3a** (0.0886 g, 0.805 mmol), and methanol (5 mL). An identical reaction but with a chromatographic workup of the methanol phase (20 × 2.5 cm silica gel column, CHCl₃ elution) gave yellow **4a** (0.0782 g, 0.723 mmol, 90%) that was pure by ¹H NMR, and **1-R_{f10}** (0.5136 g, 0.7950 mmol, 99%).

A flask was similarly charged with **2-R_{f10}** (0.4722 g, 0.5415 mmol; prepared from the **1-R_{f10}** from the previous cycle; 68% yield),^{s1} **3a** (0.0595 g, 0.540 mmol), and methanol (5 mL). An identical reaction and workup gave yellow **4a** (0.0537 g, 0.497 mmol, 92%) that was pure by ¹H NMR, and **1-R_{f10}** (0.3458 g, 0.5353 mmol, 99%).

D. (Chart 3) A vial was charged with **2-R_{f10}** (1.020 g, 1.169 mmol), **3a** (0.116 g, 1.05 mmol), and methanol/H₂O (10:1 v/v; 5 mL). The suspension was stirred and immediately turned yellow; a new white solid formed. After 1 h, the mixture was centrifuged. The yellow supernatant was decanted and the precipitate washed with methanol/H₂O (10:1 v/v; 3 mL) and centrifuged (3 ×). The methanol phases were combined and extracted with hexane (2 × 5 mL), and the extract was added to the precipitate. The resulting solution was extracted with methanol/H₂O (10:1 v/v; 2 × 5 mL). Solvent was then removed by rotary evaporation to give **1-R_{f10}** (0.731 g, 1.13 mmol, 97%). The combined methanol/H₂O solutions were concentrated (to ca. 2 mL) and chromatographed (20 × 2.5 cm silica gel column, CHCl₃ elution). Solvent was removed from the yellow fractions to give **4a** (0.114 g, 1.05 mmol, >99%) that contained 2% of **3a** by ¹H NMR.

A vial was similarly charged with **2-R_{f10}** (0.619 g, 0.710 mmol; prepared from the **1-R_{f10}** from the previous cycle; 63% yield),^{s1} **3a** (0.0710 g, 0.650 mmol), and methanol/H₂O (10:1 v/v; 5 mL). An identical reaction and workup gave (lightly-green)-yellowish **4a** (0.0691 g, 0.650 mmol, >99%) that contained 12% of **3a** by ¹H NMR, and **1-R_{f10}** (0.427 g, 0.661 mmol, 93%).

A vial was similarly charged with **2-R_{f10}** (0.381 g, 0.437 mmol; prepared from the **1-R_{f10}** from the previous cycle; 66% yield),^{s1} **3a** (0.0450 g, 0.410 mmol), and methanol/H₂O (10:1 v/v; 5 mL). An identical reaction and workup gave (lightly-green)-yellowish **4a** (0.0441 g, 0.410 mmol, >99%) that contained 8% of **3a** by ¹H NMR, and **1-R_{f10}** (0.278 g, 0.430 mmol, 98%).

E. (Chart 4) A vial was charged with **2-R_{f12}** (0.498 g, 0.509 mmol), **3a** (0.0450 g, 0.410 mmol), and methanol (5 mL). The suspension was stirred and immediately turned yellow; a new white solid formed. After 1 h, the mixture was centrifuged. The yellow supernatant was decanted. The precipitate was washed with methanol (3 × 2 mL, with centrifugation) and dried by rotary evaporation to give **1-R_{f12}** (0.365 g, 0.489 mmol, 95%). The methanol phases were combined. The solvent was removed by rotary evaporation to give green-yellowish **4a** (0.0443 g, 0.410 mmol, >99%) that contained 9% of **3a** by ¹H NMR.

A vial was similarly charged with **2-R_{f12}** (0.426 g, 0.440 mmol; prepared from the **1-R_{f12}** from the previous cycle; 90% yield), **3a** (0.0381 g, 0.345 mmol) and methanol (5 mL). An identical reaction and workup gave green-yellowish **4a** (0.0372 g, 0.345 mmol, >99%) that contained 15% of **3a** by ¹H NMR and **1-R_{f12}** (0.293 g, 0.393 mmol, 89.6%).

A vial was similarly charged with **2-R_{f12}** (0.341 g, 0.351 mmol; prepared from the **1-R_{f12}** from the previous cycle; 89% yield), **3a** (0.0299 g, 0.272 mmol) and methanol (5 mL). An identical reaction and workup gave greenish **4a** (0.0295 g, 0.272 mmol, >99%) that contained 25% of **3a** by ¹H NMR and **1-R_{f12}** (0.249 g, 0.334 mmol, 95%).

Partition Coefficients. A. A 5 mL vial was charged with **1-R_{f8}** (0.0650 g, 0.119 mmol), CF₃C₆F₁₁ (2.00 mL), and methanol (2.00 mL). The mixture was vigorously shaken (2 min) and immersed in a 35 °C oil bath. After 12 h, the bath was removed. After 12 h, a 0.200 mL aliquot of each layer of was added to 0.100 mL of a standard 0.0138 M solution of undecane in hexane. The samples were diluted with ether and GC analysis (average of three injections) showed 0.0105 mmol of **1-R_{f8}** in the CF₃C₆F₁₁ aliquot and 0.00125 mmol in the methanol aliquot (89.4:10.6; a 2.00/0.200 scale factor gives a total mass recovery of 0.0642 g, 0.118 mmol, 99%). **B.** A 5 mL vial was charged with **1-R_{f10}** (0.0881 g, 0.136 mmol), CF₃C₆F₁₁ (2.00 mL), and methanol (2.00 mL). The mixture was vigorously shaken (2 min) and immersed in a 35 °C oil bath. After 12 h, the bath was removed. After 12 h, a 0.500 mL aliquot of each layer was added to 0.200 mL of a standard 0.0138 M solution of undecane in hexane. The samples were diluted with ether and GC analysis (average of three injections) showed 0.0322 mmol of **1-R_{f10}** in the CF₃C₆F₁₁ aliquot and 0.00078 mmol in the methanol aliquot (97.6:2.4; a 2.00/0.500 scale factor gives a total mass recovery of 0.0852 g, 0.132 mmol 97%).

(s1) **CAUTION:** Concentrated H_2O_2 may decompose violently in contact with iron, copper, chromium, and most other metals and their salts and dust. Absolute cleanliness, suitable equipment (uncontaminated PVC, butyl or Neoprene rubber, Teflon[®]), and personal protection are essential for safe handling. See *Bretherick's Handbook of Reactive Chemical Hazards*, 6th ed, Urben, P. G. Ed.; Butterworth Heinemann, Boston, 1999.

(s2) Huckaba, C. E.; Keyes, F. G. *J. Am. Chem. Soc.* **1948**, *70*, 1640.

(s3) The mass spectra of iodine(III) compounds often show signals for di(iodine) species: Silva, L. F. Jr.; Lopez, N. P. *Tetrahedron Lett.* **2005**, *46*, 6023.

(s4) The triplets of the CF_3 groups represent $^4J_{\text{FF}}$ and not $^3J_{\text{FF}}$ values; see (a) White, H. F. *Anal. Chem.* **1968**, *38*, 625. (b) Foris, A. *Magn. Reson. Chem.* **2004**, *42*, 534.

(s5) The greater excess of oxidizing agent helps to solubilize the $\mathbf{1-R}_{\text{f}10}$ or $\mathbf{1-R}_{\text{f}12}$, increasing the rate and effectiveness of the oxidation.

(s6) Rocaboy, C.; Gladysz, J. A. *Chem. Eur. J.* **2003**, *9*, 88.