Supporting Information
for
2-Iodo-N-isopropyl-5-methoxybenzamide as a highly reactive and environmentally benign catalyst for alcohol oxidation

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Experimental details and the ¹H and ¹³C NMR spectra of the catalysts, the substrates, and the products

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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 JEOL FT/IR-460Plus spectrometer. All NMR spectra were recorded using JEOL ECX-400P or JEOL 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), CD₃CN (= 1.93 ppm, solvent residual signal), or DMSO-d₆ (= 2.49 ppm, solvent residual signal). For ¹³C NMR, the reference point is CDCl₃ (= 77.0 ppm), CD₃CN (= 1.3 ppm), or DMSO-d₆ (= 39.7 ppm). Electron ionization (EI) mass spectra were recorded using a JEOL JMS-GCmate II 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

Preparation of catalyst

4-Iodo-N-isopropylbenzamide (16)

A solution of 4-iodobenzoic acid (248 mg, 1.0 mmol) in thionyl chloride (1.25 mL) was heated at reflux with stirring for 2 h. The resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH$_2$Cl$_2$ (3.3 mL). To the mixture were added isopropylamine (71 mg, 1.2 mmol) and triethylamine (304 mg, 3.0 mmol) at 0 ºC under a nitrogen atmosphere. After stirring at room temperature for 17 h, the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO$_3$, water, and brine; dried over Na$_2$SO$_4$; filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl$_3$ to give 16 (105 mg, 36% in 2 steps) as colorless needles: mp 175–176 ºC (hexane/CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79–7.76 (2H, m), 7.49–7.46 (2H, m), 5.86 (1H, br s), 4.33–4.21 (1H, m), 1.26 (6H, d, $J$ = 6.9 Hz). The data were in accordance with the literature values [1].

2-Iodo-N-isopropyl-5-methoxybenzamide (17)

A solution of sodium nitrite (1.56 g, 22.5 mmol) in water (4.5 mL) was added dropwise to a solution of 2-amino-5-hydroxybenzoic acid (2.30 g, 15.0 mmol) in a mixture of water (20 mL) and concentrated sulfuric acid (2.8 mL) at 0 ºC. After stirring for 5 min, a solution of potassium iodide (3.74 g, 22.5 mmol) in water (4.5 mL) was added dropwise to the mixture. The resulting solution was heated at 100 ºC with stirring for 1 h and then allowed to cool to room temperature. After stirring for 14 h, the mixture was cooled to 0 ºC. The precipitate was collected by filtration, washed with cold water, and dried in vacuo to give crude 5-hydroxy-2-iodobenzoic acid (3.26 g) as a brown solid, which was dissolved in anhydrous DMF (65 mL). To this solution were added potassium carbonate (12.8 g, 92.7 mmol) and iodomethane (5.8 mL, 92.7 mmol) at room temperature under a nitrogen atmosphere. After stirring for 12 h, the mixture was filtered through a pad of celite and the pad was washed with Et$_2$O. The filtrate was acidified with 10% HCl and then extracted with Et$_2$O. The organic layer was washed with saturated aqueous NaHCO$_3$, water, and brine, dried over Na$_2$SO$_4$; filtered; and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 4/1) to give methyl 2-iodo-5-methoxybenzoate [2] (3.44 g, 79% in 2 steps) as a pale yellow oil: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.83 (1H, d, $J$ = 8.6 Hz), 7.35 (1H, d, $J$ = 2.9 Hz), 6.75 (1H, dd, $J$ = 8.6, 2.9 Hz), 3.93 (3H, s), 3.82 (3H, s). To a solution of methyl 2-iodo-5-methoxybenzoate (1.21 g, 4.13 mmol) in a 3:1 mixture of MeOH and water (47 mL) was added lithium hydroxide hydrate (260 mg, 6.2 mmol) at room temperature. After stirring for 15 h, the resulting mixture was diluted with saturated aqueous NaHCO$_3$ and washed with CH$_2$Cl$_2$. The aqueous layer was acidified with 10% HCl and then extracted with Et$_2$O. The last organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was dissolved in thionyl chloride (5.1 mL). After heating at reflux with stirring for 2 h, the resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH$_2$Cl$_2$ (13.5 mL). To the mixture were added isopropylamine (290 mg, 4.9 mmol) and triethylamine (1.24 g, 12.2 mmol) at 0 ºC under a nitrogen atmosphere. After stirring at room temperature for 6 h, the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO$_3$, water, and brine; dried over Na$_2$SO$_4$; filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl$_3$ to give 17 (3.42 g, 79% in 2 steps) as a white solid: mp 207–208 ºC (hexane/CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.73–8.68 (2H, m), 7.49–7.36 (4H, m), 7.02–6.95 (2H, m), 6.73 (1H, d, $J$ = 8.6 Hz), 3.85–3.78 (6H, m), 3.69 (3H, s), 3.58 (3H, s).
pressure. The residue was purified by recrystallization from hexane and CHCl₃ to give 17 (991 mg, 75% in 3 steps) as colorless needles: mp 147–148.5 °C (hexane/CHCl₃); IR (KBr) ν 3278, 2972, 1640, 1584, 1542, 1468, 1391, 1351, 1312, 1278, 1262, 1236, 1146, 1114, 1041, 1012, 927, 867, 816, 798, 714 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.68 (1H, d, J = 8.6 Hz), 6.96 (1H, d, J = 2.9 Hz), 6.68 (1H, dd, J = 8.6, 2.9 Hz), 5.61 (1H, br d, J = 6.3 Hz), 4.34–4.24 (1H, m), 3.80 (3H, s), 1.29 (6H, d, J = 6.3 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 168.2, 159.7, 143.2, 140.4, 117.6, 114.0, 80.6, 55.5, 42.2, 22.6; HRMS (EI) calcld for C₁₀H₈INO₂ ([MI⁺]: 319.0070; found 319.0060.

2-Iodo-N-isopropyl-5-methylbenzamide (18)

A solution of sodium nitrite (513 mg, 7.44 mmol) in water (3.7 mL) was added dropwise to a solution of 2-amino-5-methylbenzoic acid (562 mg, 3.72 mmol), acetone (3.1 mL), and concentrated HCl (1.8 mL) at 0 °C. After stirring for 2 h, potassium iodide (1.24 g, 7.44 mmol) was added to the mixture. The resulting solution was stirred at 0 °C for 0.5 h, heated at 90 °C for 10 min, and then allowed to cool to room temperature. The mixture was extracted with CHCl₃. The organic layer was washed with saturated aqueous Na₂S₂O₃ and water, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 4/1) to give 2-iodo-5-methylbenzoic acid [3] (829 mg, 85%) as a colorless solid: ¹H NMR (400 MHz, CDCl₃) δ 7.91 (1H, d, J = 8.2 Hz), 7.84 (1H, d, J = 1.8 Hz), 7.02 (1H, dd, J = 8.2, 1.8 Hz), 2.36 (3H, s). To a solution of 2-iodo-5-methylbenzoic acid (252 mg, 0.96 mmol) was added thionyl chloride (1.2 mL). After heating at reflux with stirring for 2 h, the resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH₂Cl₂ (3 mL). To the mixture were added isopropylamine (68 mg, 1.15 mmol) and triethylamine (291 mg, 2.88 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 6 h, the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO₃, water, and brine; dried over Na₂SO₄; filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl₃ to give 18 (203 mg, 70% in 2 steps) as colorless needles: mp 147–149 °C (hexane/CHCl₃); IR (KBr) ν 3278, 2972, 1640, 1591, 1568, 1540, 1465, 1455, 1363, 1346, 1302, 1266, 1221, 1170, 1159, 1147, 1130, 1017, 922, 885, 856, 810, 797, 778, 721, 692, 666 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (1H, d, J = 8.2 Hz), 7.21 (1H, d, J = 2.3 Hz), 6.92–6.89 (1H, m), 5.54 (1H, br s), 4.35–4.23 (1H, m), 2.31 (3H, s), 1.29 (6H, d, J = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 142.2, 139.4, 138.3, 131.9, 129.1, 88.2, 42.1, 22.6, 20.8; HRMS (EI) calcld for C₁₁H₁₂INO ([MI⁺]: 303.0120; found 303.0093.

5-Chloro-2-iodo-N-isopropylbenzamide (19)

According to the procedure reported by Yu and co-workers [3], palladium acetate (22 mg, 0.10 mmol), iodobenzene diacetate (644 mg, 2.0 mmol), iodine (507 mg, 2.0 mmol), and tetrabutylammonium iodine (739 mmol, 2.0 mmol) were added to a solution of 3-chlorobenzoic acid (313 mg, 2.0 mmol) in 1,2-dichloroethane (20 mL). The mixture was heated at 100 °C with stirring for 2 h and then allowed to cool to room temperature. Iodobenzene diacetate (644 mg, 2.0 mmol) and iodine (507 mg, 2.0 mmol) were added to the mixture. After stirring at 100 °C for 4 h, the resulting mixture was diluted with 10% sodium carbonate. The aqueous layer was separated, washed with Et₂O, and then acidified with 10% HCl. The resulting mixture was extracted with EtOAc and the organic layer was dried over Na₂SO₄; filtered; and concentrated.
under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 4/1) to give crude 5-chloro-2-iodobenzoic acid (223 mg) as a colorless solid, which was suspended in thionyl chloride (2 mL). After stirring under reflux conditions for 2 h, the resulting mixture was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CHCl₃ (3 mL). To the mixture were added isopropylamine (56 mg, 0.95 mmol) and triethylamine (240 mg, 2.37 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 13 h, the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO₃, water, and brine; dried over Na₂SO₄; filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl₃ to give 19 (138 mg, 21% in 3 steps) as colorless needles: mp 160.5–162 °C (hexane/CHCl₃); IR (KBr) ν 3259, 2972, 1641, 1577, 1546, 1452, 1378, 1343, 1304, 1261, 1155, 1096, 1020, 884, 814, 725 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (1H, d, J = 8.7 Hz), 7.37 (1H, d, J = 2.8 Hz), 7.08 (1H, dd, J = 8.7, 2.8 Hz), 5.54 (1H, br s), 4.34–4.23 (1H, m), 1.29 (6H, d, J = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 167.2, 143.8, 140.8, 134.7, 131.1, 128.3, 89.5, 42.4, 22.5; HRMS (EI) calcd for C₁₀H₁₁ClINO ([M⁺⁺): 322.9574; found 322.9580.

5-Acetoxy-2-iodo-N-isopropylbenzamide (20)

To a solution of 5-hydroxy-2-iodobenzoic acid (264 mg, 1.0 mmol) in pyridine (0.57 mL) was added acetic anhydride (410 mg, 4.0 mmol) at room temperature under a nitrogen atmosphere. After stirring for 1 h, the resulting mixture was acidified with 10% HCl and then extracted with EtOAc. The organic layer was washed with 10% HCl and brine; dried over Na₂SO₄; filtered; and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 1/1) to give 5-acetoxy-2-iodobenzoic acid [3] (296 mg, 97%) as a colorless crystalline solid; IR (KBr) ν 3240, 3064, 2970, 1756, 1628, 1556, 1459, 1366, 1330, 1216, 1203, 1175, 1012, 947, 914, 822, 724 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (1H, d, J = 8.7 Hz), 7.37 (1H, d, J = 2.8 Hz), 7.02 (1H, dd, J = 8.7, 2.8 Hz), 2.33 (3H, s). To a solution of 5-acetoxy-2-iodobenzoic acid (296 mg, 0.97 mmol) was added thionyl chloride (2 mL). After heating at reflux with stirring for 3 h, the resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH₂Cl₂ (3 mL). To the mixture were added isopropylamine (69 mg, 1.16 mmol) and triethylamine (294 mg, 2.91 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 14 h, the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO₃, water, and brine; dried over Na₂SO₄; filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl₃ to give 20 (138 mg, 41% in 2 steps) as colorless needles: mp 143–144.5 °C (hexane/CHCl₃); IR (KBr) ν 3240, 3064, 2970, 1756, 1638, 1556, 1459, 1366, 1330, 1216, 1203, 1175, 1012, 947, 914, 822, 724 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (1H, d, J = 8.7 Hz), 7.13 (1H, d, J = 2.8 Hz), 6.86 (1H, dd, J = 8.7, 2.8 Hz), 5.71 (1H, br d, J = 7.3 Hz), 4.32–4.20 (1H, m), 2.29 (3H, s), 1.27 (6H, d, J = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 168.9, 167.4, 150.7, 143.5, 140.6, 124.5, 121.7, 88.1, 42.2, 22.5, 21.0; HRMS (EI) calcd for C₁₂H₁₃INO₃ ([M⁺⁺): 347.0019; found 347.0027.

2-Iodo-N-isopropyl-5-methoxycarboxylbenzamide (21)

A solution of sodium nitrite (75 mg, 1.08 mmol) in water (0.54 mL) was added dropwise to a solution of 2-amino-5-methoxycarboxylbenzoic acid [4] (106 mg, 0.55 mmol) in a 7:3:1 mixture of water (1.9 mL), acetone (0.8 mL), and concentrated HCl (0.26 mL). After stirring

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for 2 h, potassium iodide (179 mg, 1.08 mmol) was added to the mixture. The resulting mixture was stirred at 0 °C for 0.5 h and then allowed to warm to room temperature. The mixture was extracted with CHCl₃. The organic layer was washed with water, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluents: hexane/EtOAc = 4/1) to give methyl 2-iodo-5-methoxycarbonylbenzoic acid [3] (130 mg, 77%) as a colorless solid: ¹H NMR (400 MHz, CDCl₃) δ 8.64 (1H, d, J = 1.8 Hz), 8.17 (1H, d, J = 8.2 Hz), 7.83 (1H, dd, J = 8.2, 1.8 Hz), 3.96 (3H, s). A solution of 2-iodo-5-methoxycarbonylbenzoic acid (118 mg, 0.39 mmol) in thionyl chloride (1.5 mL) was heated at reflux with stirring for 2 h. The resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH₂Cl₂ (1.3 mL). To the mixture were added isopropylamine (28 mg, 0.47 mmol) and triethylamine (121 mg, 1.2 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 1 h, the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO₃, water, and brine; dried over Na₂SO₄; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl₃ to give 21 (65 mg, 48% in 2 steps) as colorless prisms: mp 170–171.5 °C (hexane/CHCl₃); IR (KBr) ν 3271, 3087, 2978, 2958, 2936, 1732, 1641, 1589, 1542, 1454, 1435, 1391, 1367, 1350, 1281, 1245, 1196, 1154, 1128, 1109, 1016, 984, 918, 905, 853, 840, 815, 757, 725, 689, 656 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (1H, d, J = 2.3 Hz), 7.95 (1H, d, J = 8.2 Hz), 7.70 (1H, dd, J = 8.2, 2.3 Hz), 5.63 (1H, br d, J = 6.9 Hz), 4.36–4.24 (1H, m), 3.92 (3H, s), 1.30 (6H, d, J = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 165.9, 142.8, 140.1, 131.3, 130.2, 128.7, 98.8, 52.5, 42.3, 22.6; HRMS (EI) calcld for C₁₇H₁₄INO₃ ([M]+): 347.0019; found 347.0015.

2-Iodo-N-isopropyl-5-nitrobenzamide (22)

2-Amino-5-nitrobenzoic acid (500 mg, 2.75 mmol) was dissolved in 0.5 M NaOH (5 mL) at 70 °C. The resulting solution was allowed to cool to 0 °C and the treated with concentrated HCl (1 mL). To the mixture was added dropwise a solution of sodium nitrite (196 mg, 2.84 mmol) in water (2.5 mL). After stirring for 0.5 h, a solution of potassium iodide (913 mg, 5.5 mmol) in 0.5 M NaOH (5 mL). To the mixture was added dropwise a solution of sodium nitrite (196 mg, 2.84 mmol) in water (2.5 mL). After stirring for 0.5 h, a solution of potassium iodide (913 mg, 5.5 mmol) in water (2.5 mL) was added dropwise to the mixture. The resulting solution was stirred for 1 h and allowed to warm to room temperature. After stirring for 12 h, the precipitate was collected by filtration, washed with water, and dried in vacuo. The residue was purified by silica gel column chromatography (eluents: hexane/EtOAc = 1/1) to give 5-nitro-2-iodobenzoic acid [5] (453 mg, 56%) as a pale yellow solid: ¹H NMR (400 MHz, CDCl₃) δ 8.80 (1H, d, J = 2.8 Hz), 8.29 (1H, d, J = 8.7 Hz), 8.03 (1H, dd, J = 8.7, 2.8 Hz). A solution of 5-nitro-2-iodobenzoic acid (293 mg, 1.0 mmol) in thionyl chloride (1.3 mL) was heated at reflux with stirring for 2 h. The resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH₂Cl₂ (3.3 mL). To the mixture were added isopropylamine (71 mg, 1.2 mmol) and triethylamine (304 mg, 3.0 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 21 h, the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO₃, water, and brine; dried over Na₂SO₄; filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl₃ to give 22 (69 mg, 21% in 2 steps) as colorless needles: mp 196–198 °C (hexane/CHCl₃); IR (KBr) ν 3262, 3087, 2972, 1643, 1606, 1538, 1454, 1351, 1304, 1153, 1021, 905, 864, 839, 826, 737, 730 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (1H, d, J = 2.8 Hz), 8.07 (1H, d, J = 8.7 Hz), 7.92 (1H, dd, J = 8.7, 2.3 Hz), 4.24 (1H, d, J = 6.4 Hz), 3.92 (3H, s), 2.59 (6H, s, J = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 171.6, 165.9, 142.8, 140.1, 131.3, 130.2, 128.7, 98.8, 52.5, 42.3, 22.6; HRMS (EI) calcld for C₁₇H₁₆INO₃ ([M]+): 351.0140; found 351.0145.
2.8 Hz), 5.64 (1H, br d, J = 6.0 Hz), 4.38–4.26 (1H, m), 1.32 (6H, d, J = 6.9 Hz); \(^\text{13}^\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.4, 147.8, 143.9, 141.1, 124.9, 122.6, 101.0, 42.6, 22.5; HRMS (EI) calcd for C\(_{16}\)H\(_{12}\)N\(_2\)O\(_3\) ([M]+): 333.9815; found 333.9812.

2-ido-N-isopropyl-4-methoxybenzamide (24)

A solution of sodium nitrite (105 mg, 1.52 mmol) in water (0.76 mL) was added dropwise to a solution of 2-amino-4-methoxybenzoic acid (127 mg, 0.76 mmol) in a mixture of water (1.9 mL), acetone (0.6 mL), and concentrated HCl (0.4 mL) at 0 °C. After stirring for 2 h, potassium iodide (252 mg, 1.52 mmol) was added to the mixture. The resulting solution was stirred at 0 °C for 0.5 h, heated at 90 °C for 10 min, and then allowed to cool to room temperature. The mixture was extracted with CHCl\(_3\). The organic layer was washed with saturated aqueous Na\(_2\)SO\(_4\) and water, dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure to give crude 2-ido-4-methoxybenzoic acid (829 mg) as a colorless solid, which was suspended in thionyl chloride (1.6 mL). The mixture was heated at reflux with stirring for 2 h. The resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH\(_2\)Cl\(_2\) (2.2 mL). To the mixture were added isopropylamine (46 mg, 0.78 mmol) and triethylamine (197 mg, 1.95 mmol) at 0 °C. After stirring for 2 h, the mixture was extraced with CHCl\(_3\), saturated aqueous NaHCO\(_3\), water, and brine; dried over Na\(_2\)SO\(_4\); filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl\(_3\) to give 24 (97 mg, 40% in 3 steps) as colorless needles: mp 132.5–135 °C (hexane/CHCl\(_3\)); IR (KBr) \(\nu\) 3299, 2971, 2938, 1635, 1597, 1541, 1484, 1467, 1456, 1440, 1348, 1288, 1231, 1177, 1035, 1024, 881, 847, 822, 798, 773 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (1H, d, J = 2.3 Hz), 7.35 (1H, d, J = 8.7 Hz), 6.89 (1H, dd, J = 8.7, 2.3 Hz), 5.58 (1H, br d, J = 5.0 Hz), 4.34–4.22 (1H, m), 3.80 (3H, s) 1.28 (6H, d, J = 6.4 Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.1, 160.5, 134.7, 129.3, 125.0, 114.0, 92.9, 55.6, 42.2, 22.6; HRMS (EI) calcd for C\(_{16}\)H\(_{12}\)INO\(_3\) ([M]+): 319.0070; found 319.0078.

2-ido-N-isopropyl-3-methoxybenzamide (25)

A solution of sodium nitrite (166 mg, 2.4 mmol) in water (1.2 mL) was added dropwise to a solution of 2-amino-3-methoxybenzoic acid (201 mg, 1.2 mmol) in a mixture of water (3 mL), acetone (1 mL), and concentrated HCl (0.6 mL) at 0 °C. After stirring for 2 h, potassium iodide (398 mg, 2.4 mmol) was added to the mixture. The resulting solution was stirred at 0 °C for 0.5 h, heated at 90 °C for 10 min, and then allowed to cool to room temperature. The mixture was extracted with CHCl\(_3\). The organic layer was washed with saturated aqueous Na\(_2\)SO\(_4\) and water, dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl\(_3\) to give 25 (187 mg, 56%) as a colorless solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 (1H, dd, J = 8.2, 1.4 Hz), 7.39 (1H, dd, J = 8.2, 1.4 Hz), 3.94 (3H, s). A solution of 2-ido-3-methoxybenzoic acid (181 mg, 0.65 mmol) in thionyl chloride (1.6 mL) was heated at reflux with stirring for 2 h. The resulting solution was concentrated under reduced pressure. The remaining thionyl chloride was removed by azeotropic distillation with benzene. The residue was dissolved in anhydrous CH\(_2\)Cl\(_2\) (2.2 mL). To the mixture were added isopropylamine (46 mg, 0.78 mmol) and triethylamine (197 mg, 1.95 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 17 h,
the resulting solution was diluted with EtOAc. The mixture was washed with 10% HCl, saturated aqueous NaHCO₃, water, and brine; dried over Na₂SO₄; filtered; and concentrated under reduced pressure. The residue was purified by recrystallization from hexane and CHCl₃ to give 25 (97 mg, 47% in 2 steps) as colorless prisms: mp 136–137.5 °C (hexane/CHCl₃); IR (KBr) ν 3281, 2975, 2934, 2840, 1632, 1561, 1540, 1465, 1418, 1354, 1331, 1300, 1264, 1201, 1171, 1153, 1128, 1062, 1014, 789, 758, 713, 687 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (1H, t, J = 7.8 Hz), 6.96 (1H, dd, J = 7.8, 0.9 Hz), 6.82 (1H, dd, J = 7.8, 0.9 Hz), 5.54 (1H, br d, J = 6.4 Hz), 4.36–4.24 (1H, m), 3.90 (3H, s), 1.28 (6H, d, J = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 158.2, 144.8, 129.7, 120.3, 111.4, 85.2, 56.7, 42.1, 22.6; HRMS (EI) calcd for C₁₁H₁₄INO₂ ([M]+): 319.0070; found 319.0069.

Typical experimental procedure for oxidation of secondary alcohols 14a–f[7]

Secondary alcohol 14 (0.50 mmol) was added to a solution of the catalyst (0.15 mmol) and Bu₄NHSO₄ (170 mg, 0.50 mmol) in a mixture of MeNO₂ (1.6 mL) and water (0.6 mL), followed by Oxone® (768 mg, 1.25 mmol) at room temperature (25 ºC). After 14 was completely consumed as indicated by TLC, the resulting mixture was diluted with EtOAc and washed with water. The organic layer was then washed with saturated aqueous Na₂S₂O₃ and saturated aqueous NaHCO₃, dried over MgSO₄; filtered; and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give pure ketone 15 and the catalyst. All ketones 15 were directly identified by comparison with the commercial samples.

Benzophenone (15a)

\[
\begin{align*}
\text{O} \\
\text{15a}
\end{align*}
\]

¹H NMR (400 MHz, CDCl₃) δ 7.82–7.79 (4H, m), 7.61–7.56 (2H, m), 7.50–7.46 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 196.7, 137.5, 132.4, 130.0, 128.2.

4,4'-Difluorobenzophenone (15b)

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{15b}
\end{align*}
\]

¹H NMR (400 MHz, CDCl₃) δ 7.84–7.79 (4H, m), 7.20–7.14 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 193.8, 165.4 (d, J = 254 Hz), 133.7 (d, J = 2.9 Hz), 132.5 (d, J = 9.6 Hz), 115.5 (d, J = 22.0 Hz).

1-Indanone (15c)

\[
\begin{align*}
\text{15c}
\end{align*}
\]

¹H NMR (400 MHz, CDCl₃) δ 7.76 (1H, d, J = 7.3 Hz), 7.59 (1H, td, J = 7.3, 1.4 Hz), 7.50–7.47 (1H, m), 7.39–7.35 (1H, m), 3.16–3.13 (2H, m), 2.71–2.68 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 207.1, 155.1, 137.0, 134.6, 127.2, 126.6, 123.7, 36.2, 25.7.

Acetophenone (15d)

\[
\begin{align*}
\text{15d}
\end{align*}
\]

¹H NMR (500 MHz, CDCl₃) δ 7.98–7.95 (2H, m), 7.58–7.55 (1H, m), 7.49–7.45 (2H, m), 2.61 (3H, s); ¹³C NMR (126 MHz, CDCl₃) δ 198.2, 137.1, 133.1, 128.5, 128.3, 26.6.
2-Phenylacetophenone (15e)

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3\text{)} & \delta 8.02–8.00 (2H, m), 7.56–7.53 (1H, m), 7.46–7.43 (2H, m), 7.34–7.31 (2H, m), 7.28–7.23 (3H, m), 4.28 (2H, s); \\
\text{C NMR (126 MHz, CDCl}_3\text{)} & \delta 197.6, 136.5, 134.5, 133.1, 128.64, 128.61, 128.57, 126.9, 45.5.
\end{align*}
\]

4-Phenyl-2-butaneone (15f)

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3\text{)} & \delta 7.29–7.25 (2H, m), 7.21–7.17 (3H, m), 2.89 (2H, t, \text{ } J = 7.5 \text{ Hz}), 2.76 (2H, t, \text{ } J = 7.5 \text{ Hz}), 2.14 (3H, s); \\
\text{C NMR (126 MHz, CDCl}_3\text{)} & \delta 207.9, 140.9, 128.5, 128.2, 126.1, 45.1, 30.0, 29.7.
\end{align*}
\]

Typical experimental procedure for oxidation of primary alcohols 14g-k [7]
Primary alcohol 14 (0.50 mmol) was added to a solution of the catalyst (0.15 mmol) and Bu₄NHSO₄ (170 mg, 0.50 mmol) in a mixture of MeNO₂ (1.6 mL) and water (0.6 mL), followed by Oxone® (768 mg, 1.25 mmol) at room temperature (25 °C). After 14 were completely consumed as indicated by TLC, the resulting mixture was diluted with EtOAc, water, and saturated aqueous Na₂S₂O₃. The organic layer was then washed with saturated aqueous Na₂S₂O₃, saturated aqueous NaHCO₃, and brine; dried over MgSO₄; filtered; and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the catalyst. The combined aqueous layers were acidified with 10% HCl and extracted with EtOAc. The organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give pure carboxylic acid 26. All carboxylic acids 26 were directly identified by comparison with the commercial samples.

4-Nitrobenzoic acid (26g)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3$/DMSO-\text{d}_{6} \text{)} & \delta 8.28 (2H, dt, \text{ } J = 8.7, 2.3 \text{ Hz}), 8.21 (2H, dt, \text{ } J = 8.7, 2.3 \text{ Hz}); \\
\text{C NMR (100 MHz, CDCl}_3$/DMSO-\text{d}_{6} \text{)} & \delta 165.2, 149.1, 135.7, 129.7, 122.3.
\end{align*}
\]

4-Chlorobenzoic acid (26h)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3$/DMSO-\text{d}_{6} \text{)} & \delta 7.99–7.95 (2H, m), 7.44–7.40 (2H, m); \\
\text{C NMR (100 MHz, CDCl}_3$/DMSO-\text{d}_{6} \text{)} & \delta 166.1, 137.5, 130.1, 128.6, 127.4.
\end{align*}
\]

Monomethyl terephthalate (26i)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3$/DMSO-\text{d}_{6} \text{)} & \delta 8.12–8.06 (4H, m), 3.94 (3H, s); \\
\text{C NMR (100 MHz, CDCl}_3$/DMSO-\text{d}_{6} \text{)} & \delta 166.8, 165.6, 134.3, 132.9, 129.0, 128.7, 51.7.
\end{align*}
\]

3-Phenylpropionic acid (26j)

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3\text{)} & \delta 7.32–7.28 (2H, m), 7.23–7.20 (3H, m), 2.97 (2H, t, \text{ } J = 8.0 \text{ Hz}), 2.69 (2H, t, \text{ } J = 8.0 \text{ Hz}); \\
\text{C NMR (126 MHz, CDCl}_3\text{)} & \delta 178.4, 140.1, 128.5, 128.2, 126.4, 35.5, 30.6.
\end{align*}
\]
Cyclohexanecarboxylic acid (26k)

\[
\begin{align*}
\text{O} & \quad \text{OH} \\
26k
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.33 (1H, t, \(J = 11.5, 4.0\) Hz), 1.97–1.91 (2H, m), 1.79–1.74 (2H, m), 1.67–1.62 (1H, m), 1.50–1.42 (2H, m), 1.34–1.19 (3H, m); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 182.4, 42.9, 28.8, 25.7, 25.3.

Preparation of 2-iodoxybenzamide

2-Iodyl-5-methoxy-N-isopropylbenzamide (29)

According to the literature [8], 0.065 M dimethyldioxirane in acetone (40 mL, 2.6 mmol) was added to a solution of 17 (275 mg, 0.86 mmol) in anhydrous CH\(_2\)Cl\(_2\) (4 mL) at room temperature under nitrogen atmosphere. After stirring for 9.5 h, the precipitate was collected by filtration, washed with anhydrous CH\(_2\)Cl\(_2\) and Et\(_2\)O, and dried in vacuo to give 29 (221 mg, 73%) as a colorless solid: mp 164 °C (dec.); IR (KBr) ν 3417 (br), 3362, 3208 (br), 3060 (br), 2975, 2942, 1623, 1609, 1588, 1572, 1553, 1467, 1440, 1400, 1362, 1318, 1300, 1251, 1187, 1172, 1142, 1028, 921, 891, 832, 773, 760 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.02 (1H, d, \(J = 7.8\) Hz), 8.17 (1H, d, \(J = 8.7\) Hz), 7.77 (1H, d, \(J = 2.8\) Hz), 7.45 (1H, dd, \(J = 8.7, 2.8\) Hz), 4.19–4.11 (1H, m), 3.90 (3H, s), 1.21 (6H, d, \(J = 6.9\) Hz); \(^1^3\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta\) 164.9, 162.0, 139.9, 130.8, 125.4, 117.7, 112.8, 56.5, 42.4, 22.2.

In situ generation of trivalent iodine derivative 27 from 29

Since the synthesis of trivalent iodine derivative 27 according to the reported synthetic procedure for 2-iodosylenzoic acid 28 [9] was unsuccessful, we examined the in situ generation of 27 by oxidation of 2-propanol to acetone with pentavalent iodine derivative 29. To a solution of 29 (2.6 mg, 7.5 μmol), KHSO\(_4\) (2.6 mg, 18.75 μmol), and Bu\(_4\)NHSO\(_4\) (2.6 mg, 7.5 μmol) in a 4:1 mixture of CD\(_3\)CN and D\(_2\)O (0.75 mL) was added 1 M 2-propanol in D\(_2\)O (15 μL, 15 μmol). The mixture was stirred at 40 °C for 143 h and the supernatant was then taken for the NMR measurement. An unknown iodine compound together with pentavalent 29 and monovalent 17 observed in the \(^1\)H NMR spectrum (Figure S1). The mixture was then kept at room temperature for ca. 4 months. The \(^1\)H NMR spectrum indicated that only 17 and the unknown iodine compound remained in the mixture. The \(^1^3\)C NMR data for 17 and the unknown iodine compound were well matched with those for 5-(n-octyloxy)-2-iodobenzoic acid and its trivalent derivative [10], respectively. Therefore, the unknown iodine compound was identified as 27.

In 27 (as a mixture with KHSO\(_4\), Bu\(_4\)NHSO\(_4\), 2-propanol, and acetone): \(^1\)H NMR (400 MHz, CD\(_3\)CN/D\(_2\)O = 4/1) \(\delta\) 7.90 (1H, d, \(J = 2.8\) Hz), 7.77 (1H, d, \(J = 9.2\) Hz), 7.57 (1H, dd, \(J = 9.2, 2.8\) Hz), 4.20 (1H, sep, \(J = 6.4\) Hz), 3.91 (3H, s), 1.26 (6H, d, \(J = 6.4\) Hz); \(^1^3\)C NMR (100 MHz, CD\(_3\)CN/D\(_2\)O = 4/1) \(\delta\) 168.3, 163.3, 129.1, 128.2, 124.1, 114.9, 109.0, 57.4, 45.7, 21.8.

In 17 (as a mixture with KHSO\(_4\) and Bu\(_4\)NHSO\(_4\)): \(^1\)H NMR (400 MHz, CD\(_3\)CN/D\(_2\)O = 4/1) \(\delta\) 7.69 (1H, d, \(J = 8.7\) Hz), 6.86 (1H, d, \(J = 3.2\) Hz), 6.73 (1H, dd, \(J = 8.7, 3.2\) Hz), 4.05 (1H, sep, \(J = 6.4\) Hz), 3.74 (3H, s), 1.17 (6H, d, \(J = 6.4\) Hz); \(^1^3\)C NMR (100 MHz, CD\(_3\)CN/D\(_2\)O = 4/1) \(\delta\) 170.1, 160.6, 144.4, 141.2, 118.0, 114.8, 81.4, 56.3, 42.8, 22.4.
Figure S1. $^1$H NMR spectra of the reaction mixture of oxidation of 2-propanol with pentavalent iodine derivatives 29.

**Oxidation of monovalent iodine derivatives to pentavalent iodine derivatives with Oxone®**

To a solution of monovalent iodine derivative 17 or 3 (7.5 μmol) and Bu$_4$NHSO$_4$ (2.6 mg, 7.5 μmol) in a 4:1 mixture of CD$_3$CN and D$_2$O (0.75 mL) was added Oxone® (11.5 mg, 18.75 μmol) at room temperature. The supernatant was taken for the NMR measurement after 12, 24, and 36 h (Figure S2 and S3). The NMR spectra of 3, 28 [9], and 2 [11] in the presence of KHSO$_4$ and Bu$_4$NHSO$_4$ in a 4:1 mixture of CD$_3$CN and D$_2$O were measured as reference.

3 (as a mixture with KHSO$_4$ and Bu$_4$NHSO$_4$): $^1$H NMR (400 MHz, CD$_3$CN/D$_2$O = 4/1) $\delta$ 7.98 (1H, d, $J$ = 7.8, 1.4 Hz), 7.76 (1H, dd, $J$ = 7.8, 1.8 Hz), 7.44 (1H, td, $J$ = 7.8, 1.4 Hz), 7.19 (1H, td, $J$ = 7.8, 1.8 Hz).

28 (as a mixture with KHSO$_4$ and Bu$_4$NHSO$_4$): $^1$H NMR (400 MHz, CD$_3$CN/D$_2$O = 4/1) $\delta$ 8.08 (1H, dd, $J$ = 7.8, 1.4 Hz), 7.92 (1H, ddd, $J$ = 8.2, 6.9, 1.4 Hz), 7.85 (1H, dd, $J$ = 8.2, 1.4 Hz), 7.69 (1H, ddd, $J$ = 7.8, 6.9, 1.4 Hz).

S10
2 (as a mixture with KHSO₄ and Bu₄NHSO₄): \(^1\)H NMR (400 MHz, CD₃CN/D₂O = 4/1) \(\delta\) 8.24 (1H, d, \(J = 7.3\) Hz), 8.14 (1H, d, \(J = 7.3\) Hz), 8.03 (1H, t, \(J = 7.3\) Hz), 7.88 (1H, t, \(J = 7.3\) Hz).

**Figure S2.** \(^1\)H NMR spectra of the reaction mixture of oxidation of 17 with Oxone\(^{\circledR}\) in the presence of Bu₄NHSO₄.
Figure S3. $^1$H NMR spectra of the reaction mixture of oxidation of 3 with Oxone® in the presence of Bu$_4$NHSO$_4$. 

3 + KHSO$_4$ + Bu$_4$NHSO$_4$

28 + KHSO$_4$ + Bu$_4$NHSO$_4$

2 (⋆) + 28 (●) + 3 (▲) + KHSO$_4$ + Bu$_4$NHSO$_4$

3 + Oxone® + Bu$_4$NHSO$_4$, 12 h

3 + Oxone® + Bu$_4$NHSO$_4$, 24 h

3 + Oxone® + Bu$_4$NHSO$_4$, 36 h
3. $^1$H and $^{13}$C NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) of 16

$^1$H NMR (500 MHz, CDCl$_3$) of 17
$^{13}$C NMR (126 MHz, CDCl$_3$) of 17

$^1$H NMR (400 MHz, CDCl$_3$) of 18
$^{13}$C NMR (100 MHz, CDCl$_3$) of 18

$^1$H NMR (400 MHz, CDCl$_3$) of 19
$^{13}$C NMR (100 MHz, CDCl$_3$) of 19

$^1$H NMR (400 MHz, CDCl$_3$) of 20
$^{13}$C NMR (100 MHz, CDCl$_3$) of 20

$^1$H NMR (400 MHz, CDCl$_3$) of 21
$^{13}$C NMR (100 MHz, CDCl$_3$) of 21

$^1$H NMR (400 MHz, CDCl$_3$) of 22
$^{13}$C NMR (100 MHz, CDCl$_3$) of 22

$^1$H NMR (400 MHz, CDCl$_3$) of 24
$^{13}$C NMR (100 MHz, CDCl$_3$) of 24

$^1$H NMR (400 MHz, CDCl$_3$) of 25
$^{13}$C NMR (100 MHz, CDCl$_3$) of 25

$^1$H NMR (400 MHz, CDCl$_3$) of 15a
$^{13}$C NMR (100 MHz, CDCl$_3$) of 15a

$^1$H NMR (400 MHz, CDCl$_3$) of 15b
$^{13}$C NMR (100 MHz, CDCl$_3$) of $15b$

$^1$H NMR (400 MHz, CDCl$_3$) of $15c$
$^{13}$C NMR (100 MHz, CDCl$_3$) of 15c

$^1$H NMR (500 MHz, CDCl$_3$) of 15d
$^{13}$C NMR (126 MHz, CDCl$_3$) of 15d

$^1$H NMR (500 MHz, CDCl$_3$) of 15e
$^{13}$C NMR (126 MHz, CDCl$_3$) of 15e

$^1$H NMR (500 MHz, CDCl$_3$) of 15f
$^{13}$C NMR (126 MHz, CDCl$_3$) of 15f

$^1$H NMR (400 MHz, CDCl$_3$/DMSO-$d_6$ = 4/1) of 26g
$^{13}$C NMR (100 MHz, CDCl$_3$/DMSO-$d_6$ = 4/1) of $26g$

$^1$H NMR (400 MHz, CDCl$_3$/DMSO-$d_6$ = 4/1) of $26h$
$^{13}$C NMR (100 MHz, CDCl$_3$/DMSO-$d_6$ = 4/1) of 26h

$^1$H NMR (400 MHz, CDCl$_3$/DMSO-$d_6$ = 4/1) of 26i
$^{13}$C NMR (100 MHz, CDCl$_3$/DMSO-$d_6 = 4/1$) of 26i

$^1$H NMR (500 MHz, CDCl$_3$) of 26j
$^{12}$C NMR (126 MHz, CDCl$_3$) of 26j

$^1$H NMR (500 MHz, CDCl$_3$) of 26k
${}^{13}$C NMR (126 MHz, CDCl$_3$) of 26k

$^1$H NMR (400 MHz, DMSO-$d_6$) of 29
$^{13}$C NMR (126 MHz, DMSO-$d_6$) of 29

$^1$H NMR (400 MHz, CD$_3$CN/D$_2$O = 4) of 29 [as a mixture with KHSO$_4$ and Bu$_4$NHSO$_4$ (▲)]
$^1$H NMR (400 MHz, CD$_3$CN/D$_2$O = 4) of 17 [as a mixture with KHSO$_4$ and Bu$_4$NHSO$_4$ (▲)]

$^{13}$C NMR (100 MHz, CD$_3$CN/D$_2$O = 4) of 17 [as a mixture with KHSO$_4$ and Bu$_4$NHSO$_4$ (▲)]
$^1$H NMR (400 MHz, CD$_2$CN/D$_2$O = 4) of 27 [as a mixture with 17, KHSO$_4$, Bu$_4$NHSO$_4$ (▲), $i$-PrOH, and acetone]

$^{13}$C NMR (100 MHz, CD$_2$CN/D$_2$O = 4) of 27 [as a mixture with 17, KHSO$_4$, Bu$_4$NHSO$_4$ (▲), $i$-PrOH, and acetone]
$^1$H NMR (400 MHz, CD$_3$CN/D$_2$O = 4) of 3 [as a mixture with KHSO$_4$ and Bu$_4$NHSO$_4$ (▲)]

$^1$H NMR (400 MHz, CD$_3$CN/D$_2$O = 4) of 28 [as a mixture with KHSO$_4$ and Bu$_4$NHSO$_4$ (▲)]
$^1$H NMR (400 MHz, CD$_3$CN/D$_2$O = 4) of 2 [as a mixture with KHSO$_4$, Bu$_4$NHSO$_4$ (▲), 3, and 28]
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