Supplementary Information

An Efficient, Catalytic, Aerobic, Oxidative Iodination of Arenes Using the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ Polyoxometalate as Catalyst

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Detailed Experimental Section

Substrates and solvents were of highest purity available and were used without further purification. The $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \times 34 \text{ H}_2\text{O}$ polyoxometalate was prepared according to a known literature method (Tsigdinos, G. A.; Hallada, C. J. *Inorg. Chem.* **1968**, 7, 437-441). Thermogravimetric analysis indicated 34 water molecules per polyoxometalate, and the elemental analysis was as follows: found (calculated) % P 1.31 (1.34), V 4.38 (4.41), Mo 41.32 (41.56). IR 1057, 960, 865, 774 cm^{-1} . ^{31}P NMR (CD_3CN , 85% H_3PO_4 external standard) -4.96 (1), -4.58 (3), -4.03 (4), -3.99 (2), -3.39 (1). Other polyoxometalates used were commercially available.

Reactions were carried out in 15 mL glass pressure tubes. In a typical procedure for activated arenes (table 1) 1 mmol arene substrate, 0.01 mmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \times 34 \text{ H}_2\text{O}$ and 0.5 mmol iodine were dissolved in 1 mL acetonitrile. Oxygen, 2 atm, was introduced to the pressure tube by two consecutive pump-thaw cycles on Schlenk line. The tubes were placed in a thermostated oil bath at 80 °C and reactions were carried out for 8 h. The reaction mixtures were then cooled; conversions and product yields were measured by GLC with both FID and MS detectors using a Restek Rtx-5MS column (5% phenylmethylsilicone, 30 m, 0.32 mm ID, 0.25 μm coating). The

regioselectivity of the reactions and confirmation of the GC analysis was carried out by ^1H NMR (400 MHz) by carrying out the reaction in CD_3CN as described above.

4-Iodo-1-methoxybenzene ^1H NMR (250 MHz, CDCl_3) δ : 3.7 (s, 3H), 6.7 (d, 2H), 7.5 (d, 2H); m/z 234 ($[\text{M}^+]$ 100%).

4-Iodo-1,2-dimethoxybenzene ^1H NMR (400 MHz, CD_3CN) δ : 3.75 (s, 3H), 3.76 (s, 3H), 6.69 (d, $J = 8$ Hz, 1H), 7.17 (d, $J = 4$ Hz, 1H), 7.21 (dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H); m/z 264 ($[\text{M}^+]$ 100%).

4-Iodo-1-methoxynaphthalene ^1H NMR (400 MHz, CD_3CN) δ : 3.88 (s, 3H), 6.57 (d, $J = 8$ Hz, 1H), 7.48 (td, $J_1 = 8$ Hz, $J_2 = 1$ Hz, 1H), 7.56 (td, $J_1 = 8$ Hz, $J_2 = 1$ Hz, 1H), 7.88 (d, $J = 8$ Hz, 1H), 7.93 (d, $J = 8$ Hz, 1H), 8.13 (d, $J = 8$ Hz, 1H); m/z 284 ($[\text{M}^+]$ 100%).

4-Iodo-1,3-dimethoxybenzene ^1H NMR (400 MHz, CD_3CN) δ : 3.79 (s, 3H), 3.84 (s, 3H), 6.38 (dd, $J_1 = 12$ Hz, $J_2 = 4$ Hz, 1H), 6.54 (d, $J = 4$ Hz, 1H), 7.62 (d, $J = 12$ Hz, 1H); m/z 264 ($[\text{M}^+]$ 100%).

1-Iodo-2-methoxynaphthalene ^1H NMR (400 MHz, CD_3CN) δ : 4.0 (s, 3H), 7.27 (d, $J = 8$ Hz, 1H), 7.41 (td, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H), 7.56 (td, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H), 7.79 (d, $J = 8$ Hz, 1H), 7.87 (d, $J = 8$ Hz, 1H), 8.11 (d, $J = 8$ Hz, 1H); m/z 284 ($[\text{M}^+]$ 100%).

4-Iodophenol ^1H NMR (400 MHz, CD_3CN) δ : 6.66 (d, $J = 8$ Hz, 2H), 7.50 (d, $J = 8$ Hz, 2H); m/z 220 ($[\text{M}^+]$ 100%).

4-Iodoaniline ^1H NMR (400 MHz, CD_3CN) δ : 3.30 (brs, 2H), 6.50 (d, $J = 8$ Hz, 2H), 7.38 (d, $J = 8$ Hz, 2H); m/z 219 ($[\text{M}^+]$ 100%).

2-Iodobenzothiophene ^1H NMR (400 MHz, CD_3CN) δ : 7.38 (t, $J = 8$ Hz, 1H), 7.45 (t, $J = 8$ Hz, 1H), 7.68 (d, $J = 8$ Hz, 1H), 7.72 (s, 1H), 7.88 (d, $J = 8$ Hz, 1H); m/z 260 ($[\text{M}^+]$ 100%).

For iodination of less reactive arenes (Table 2), 0.01 mmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \times 34 \text{H}_2\text{O}$ and 0.5 mmol iodine were dissolved in 1 mL nitrobenzene. Oxygen, 2 atm, was introduced to the pressure tube by two consecutive pump-thaw cycles on Schlenk line. The tubes were placed in a thermostated oil bath at 120 °C and reactions were carried out for 36 h. The reaction mixtures were then cooled and analyzed by GC, GC-MS and ^1H NMR as described above.

4-Iodotoluene ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 2.0 (s, 3H), 6.63 (d, $J = 8$ Hz, 2H), 7.21 (d, $J = 8$ Hz, 2H); m/z 218 ($[\text{M}^+]$ 100%).

1-Iodonaphthalene ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 6.9 (t, $J = 8$ Hz, 2H), 7.3 (t, $J = 8$ Hz, 1H), 7.49 (d, $J = 8$ Hz, 1H), 7.55 (d, $J = 8$ Hz, 1H), 7.68 (d, $J = 8$ Hz, 1H), 7.71 (d, $J = 8$ Hz, 1H); m/z 254 ($[\text{M}^+]$ 100%).

1-Iodo-4-chlorobenzene ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 6.78 (d, $J = 8$ Hz, 2H), 7.28 (d, $J = 8$ Hz, 2H); m/z 238 ($[\text{M}^+]$ 100%)

1-Iodo-2-chlorobenzene ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 6.73 (t, $J = 8$ Hz, 1H), 7.07 (t, $J = 8$ Hz, 1H), 7.14 (d, $J = 8$ Hz, 1H); 7.52 (d, $J = 8$ Hz, 1H); m/z 238 ($[\text{M}^+]$ 100%)

1-Iodo-4-bromobenzene ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 6.91 (d, $J = 8$ Hz, 2H), 7.22 (d, $J = 8$ Hz, 2H); m/z 284 ($[\text{M}^+]$ 99%)

1-Iodo-2-bromobenzene ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 6.78 (t, $J = 8$ Hz, 1H), 7.01 (t, $J = 8$ Hz, 1H), 7.3 (d, $J = 8$ Hz, 1H); 7.53 (d, $J = 8$ Hz, 1H); m/z 284 ($[\text{M}^+]$ 99%)

4-Iodobiphenyl ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 7.09 (d, $J = 8$ Hz, 2H), 7.15 (td, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H), 7.21 (td, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 2H), 7.32 (d, $J = 8$ Hz, 2H), 7.49 (dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 2H); m/z 280 ($[\text{M}^+]$ 100%)

4,4'-Diiodobiphenyl ^1H NMR (400 MHz, $\text{C}_6\text{D}_6\text{NO}_2$) δ : 7.04 (d, $J = 8$ Hz, 4H), 7.37 (d, $J = 8$ Hz, 4H); m/z 406 ($[\text{M}^+]$ 100%)

Products can be isolated as follows using the synthesis of 4-iodoanisole as an example: In a 100 mL Ace Glass pressure tube were loaded 0.324 mL (3 mmol) of anisole, 0.063 g (0.03 mmol) of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, 0.381 g (1.5 mmol) of iodine and 3 mL of acetonitrile. Oxygen was added to a pressure of 2 atm and the pressure tube was placed in an oil bath thermostated at 100 °C. After 8 hrs the pressure tube was removed from the oil bath and cooled to room temperature. The reaction mixture was diluted with 20 mL of ethylacetate and the catalyst that precipitated was separated by filtration. The resulting solution was washed with aqueous NaHSO_3 to remove traces of iodine and organic layer was separated, washed twice with saturated aqueous NaCl and dried over anhydrous Na_2SO_4 . The solvent was evaporated off by rotovap to provide 0.581 g (83%) of 4-iodoanisole. Purity: 98% (GC). Similarly isolated were for example 1-iodo-4-methoxynaphthalene 0.848 g (99.5%). Purity: 99% (GC) and 4-Iodo-1,2-dimethoxybenzene 0.75 g (95%) of 4-iodoveratrole. Purity: 98% (GC).