

Supplementary Information for

Direct Catalytic Benzene Hydroxylation under Mild Reaction Condition by Using a Monocationic μ -Nitrido-Bridged Iron Phthalocyanine Dimer with 16 Peripheral Methyl Groups

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Experimental

General

All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. A monocationic μ -nitrido-bridged iron phthalocyanine dimers ($2^+\cdot I^-$ and $1^+\cdot I^-$) and their silica gel-supported catalysts were prepared according to our previous report.^[1] 1H NMR spectra were recorded on a JEOL JNM-ECS400-A (400 MHz for 1H) spectrometer at a constant temperature of 298 K.

Benzene oxidation reaction using CH_3CN as a solvent.

Benzene oxidation was performed in a glass tube equipped with magnetic stirrer. A mixture of a solid-supported catalyst (10 mg, 47 μM as $2^+\cdot I^-$ (or $1^+\cdot I^-$)), benzene (50 μL , 481 mM), TFA (12 μL , 132 mM), and 35% aqueous H_2O_2 (100 μL , 983 mM) in CH_3CN (1.0 mL) was heated in an oil bath at a given temperature with stirring at 900 rpm for a given reaction time. After the reaction mixture was filtered through a disposable membrane filter (ADVANTEC, DISMIC-13JP), 50 μL of the resulting filtrate was mixed with 670 μL DMSO- d_6 and 80 μL of a standard solution (10 mM dimethyl sulfone in DMSO- d_6) for quantitative analysis using 1H -NMR spectroscopy.

The reaction in the presence of DMPO was performed by adding the given amount of DMPO as a solid to the reaction mixture mentioned above.

As for the oxidation of the benzene derivatives (phenol, chlorobenzene, bromobenzene, trifluoromethylbenzene, and nitrobenzene) were performed in similar manners to the method mentioned above.

In order to confirm the effectiveness and understand the intrinsic errors of the above-mentioned determination of concentrations of the oxidized products by using 1H -NMR spectroscopy, we prepared a calibration curve using 1,4-dimethoxybenzene as a standard as shown in Figure S1a. The data used for preparing this calibration curve are shown in Figure S1b. The solutions used for 1H -NMR spectroscopy were prepared by mixing an appropriate standard solution of 1,4-dimethoxybenzene (1, 2, 4, 10, 20, 40, or 100 mM) in CH_3CN (50 μL) with 670 μL DMSO- d_6 and 80 μL of a standard solution of dimethyl sulfone (10 mM in DMSO- d_6). Figure S2 shows a typical 1H -NMR spectrum used for preparing the calibration curve. As shown in Figure S1, a good correlation

coefficient ($R = 0.999$) was obtained although this method includes a relatively high deviations (up to 20%) as shown in Figure S1b.

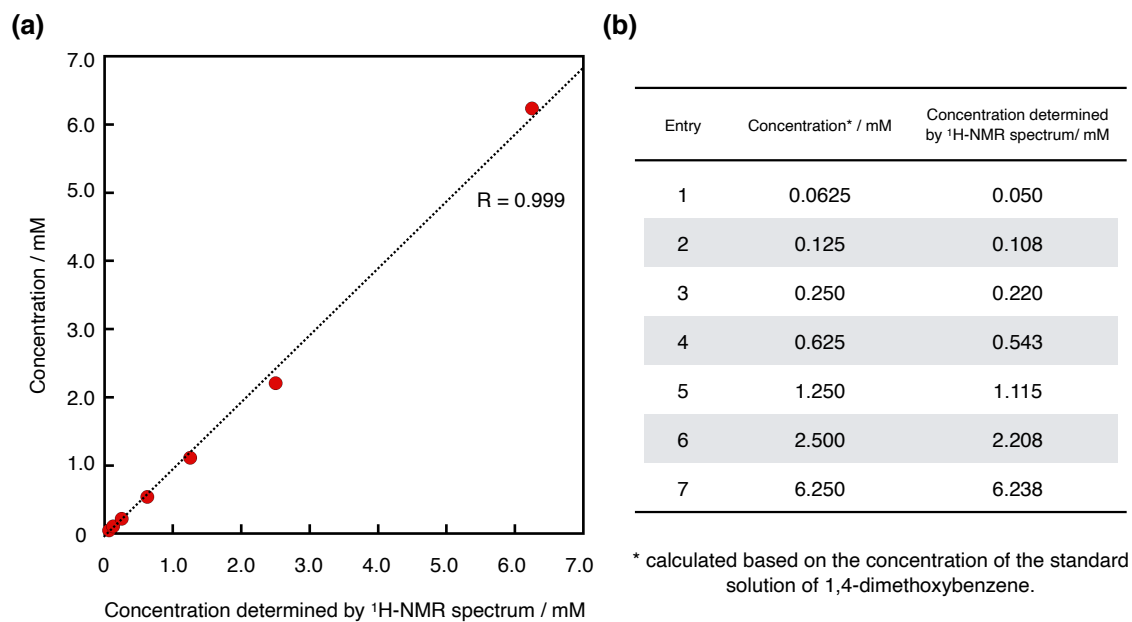


Figure S1. (a) A calibration curve to determine the concentration of 1,4-dimethoxybenzene by using $^1\text{H-NMR}$ spectroscopy. (b) A table showing the data used for preparing the calibration curve shown in Figure S1a.

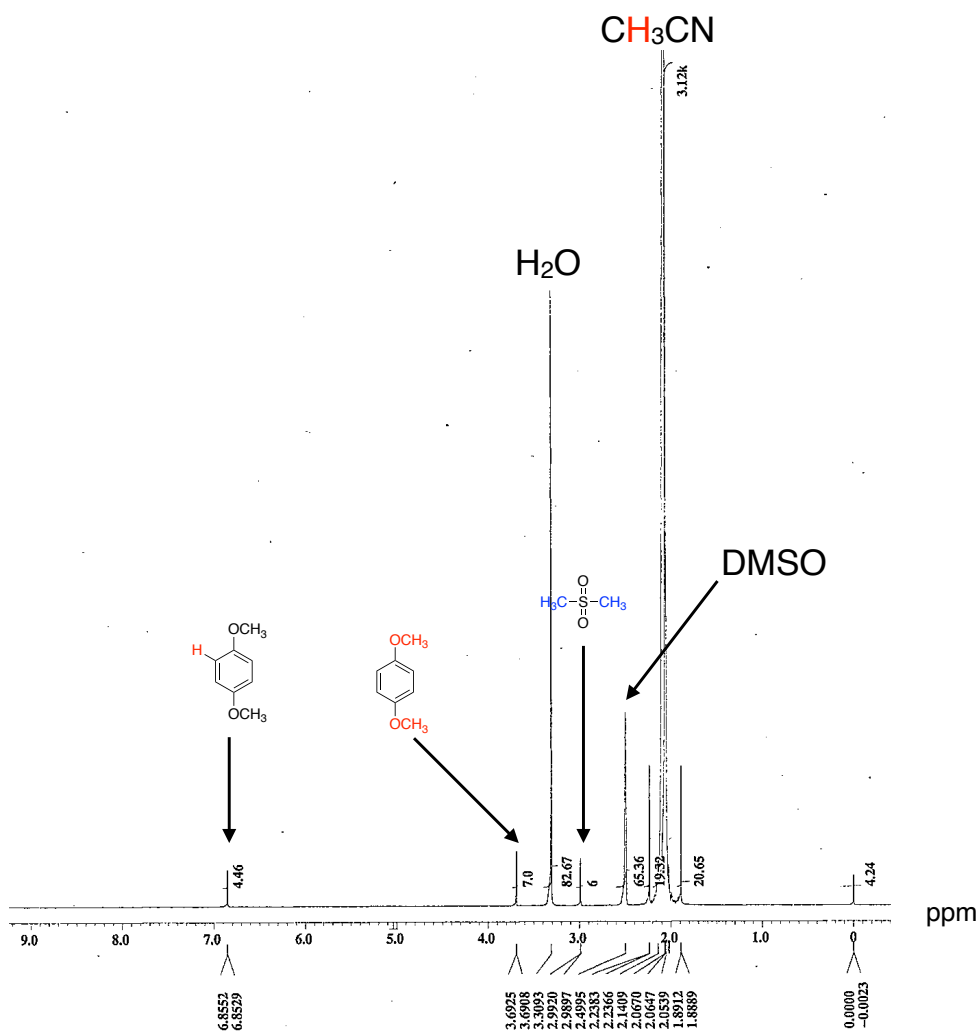


Figure S2. $^1\text{H-NMR}$ spectrum of a mixture containing 1.25 mM of 1,4-dimethoxybenzene and 1.0 mM of dimethylsulfone in a mixture of $\text{DMSO-}d_6$ and CH_3CN .

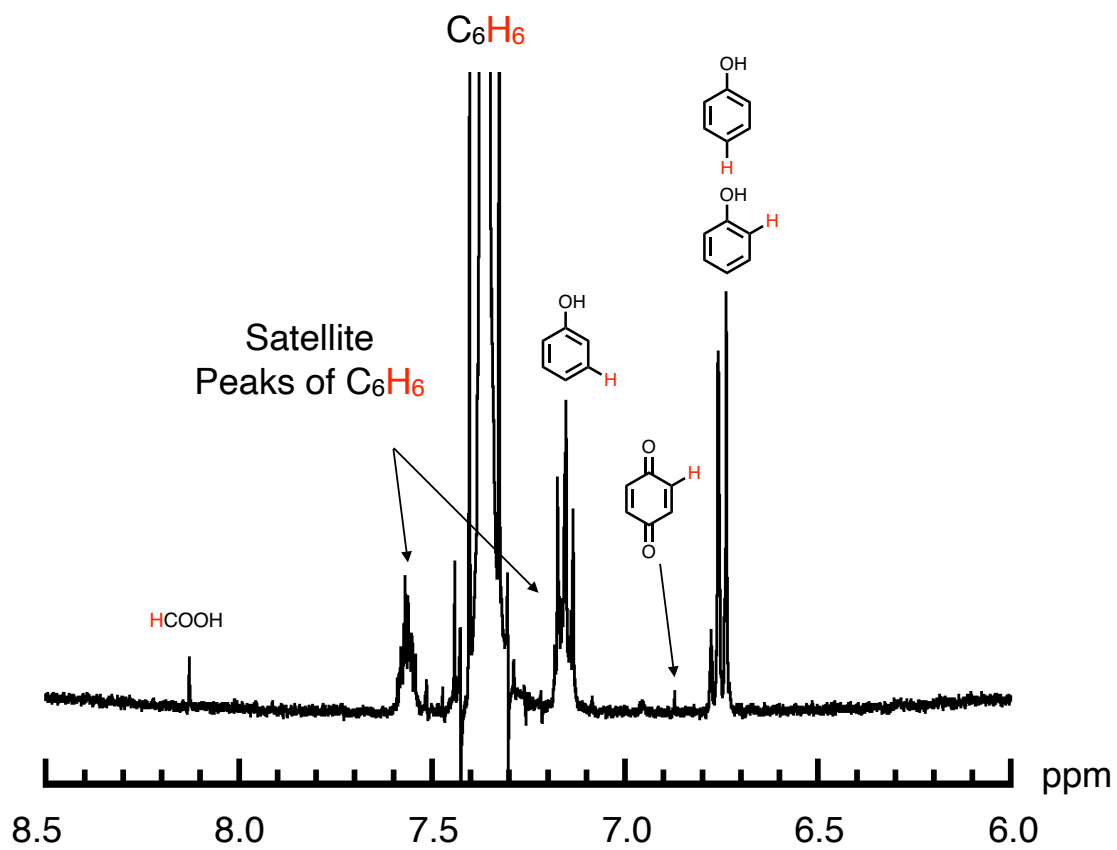


Figure S3. ^1H -NMR spectrum of the reaction mixture of benzene oxidation by $2^{+\cdot}\text{I}^-$ / SiO_2 in a CH_3CN solution containing excess H_2O_2 and TFA at 40°C for 8 h.

Benzene oxidation reaction using H₂O as a solvent. (Two-phase reaction)

Benzene oxidation in H₂O was performed in a glass tube equipped with magnetic stirrer. A mixture of a solid-supported catalyst (10 mg, 49 μM as 2⁺·I⁻), benzene (250 μL, 2.51 M), TFA (12 μL, 138 mM), and 35% aqueous H₂O₂ (100 μL, 1.03 M) in D₂O (750 μL) was heated in an oil bath at 40 °C and stirred at 900 rpm for a given reaction time. After the reaction mixture was filtered through a disposable membrane filter (ADVANTEC, DISMIC-13JP), 50 μL of the resulting filtrate was mixed with 670 μL D₂O and 80 μL of a standard solution (10 mM dimethyl sulfone in D₂O) for quantitative analysis using ¹H-NMR spectroscopy.

The concentrations of the oxidized products after 8 h reaction were determined as shown below;

Phenol : 0.651 mM

p-quinone : not detected

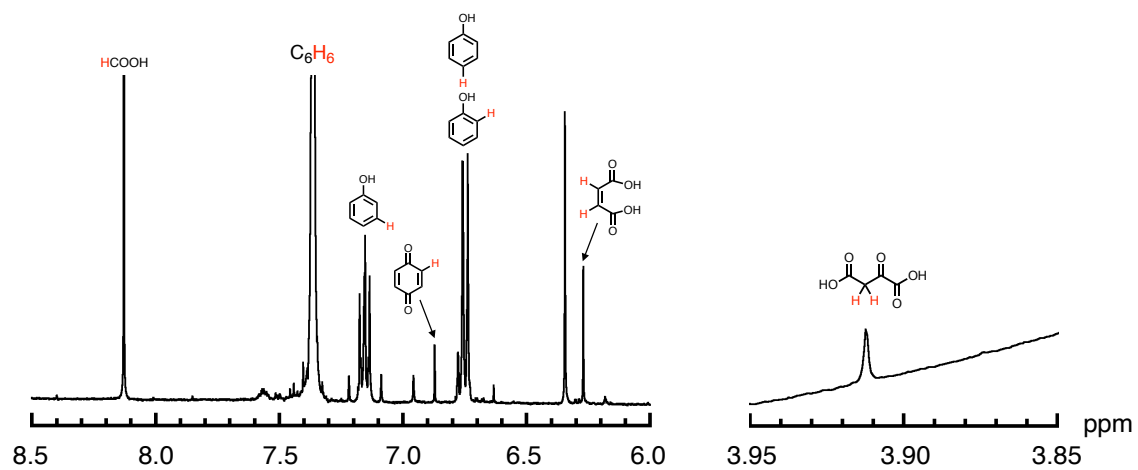


Figure S4. $^1\text{H-NMR}$ spectrum of the reaction mixture of benzene oxidation by $2^{+\cdot}\text{I}^-/\text{SiO}_2$ in a CH_3CN solution containing excess H_2O_2 and TFA at 60°C for 8 h.

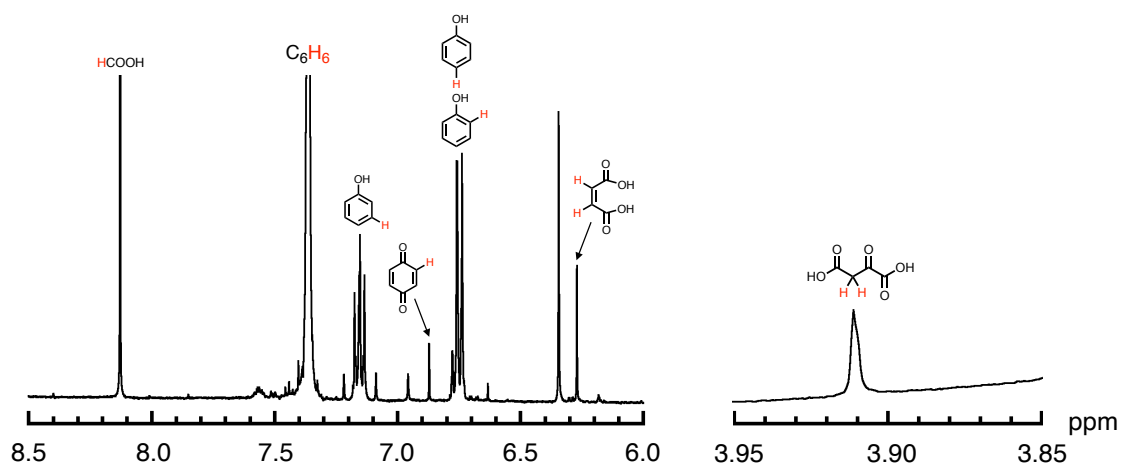


Figure S5. $^1\text{H-NMR}$ spectrum of the reaction mixture of benzene oxidation by $\mathbf{2^{+}\cdot I^{-}}$ / SiO_2 in a CH_3CN solution containing excess H_2O_2 and TFA at $80\text{ }^\circ\text{C}$ for 8 h.

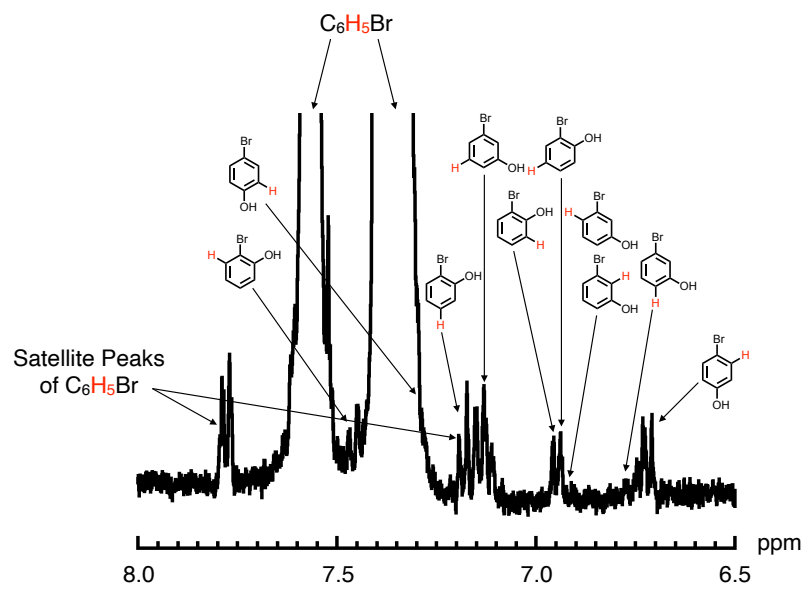


Figure S6. $^1\text{H-NMR}$ spectrum of the reaction mixture of bromobenzene oxidation by $\mathbf{2}^+\text{I}^-/\text{SiO}_2$ in a CH_3CN solution containing excess H_2O_2 and TFA at $40\text{ }^\circ\text{C}$ for 6 h.

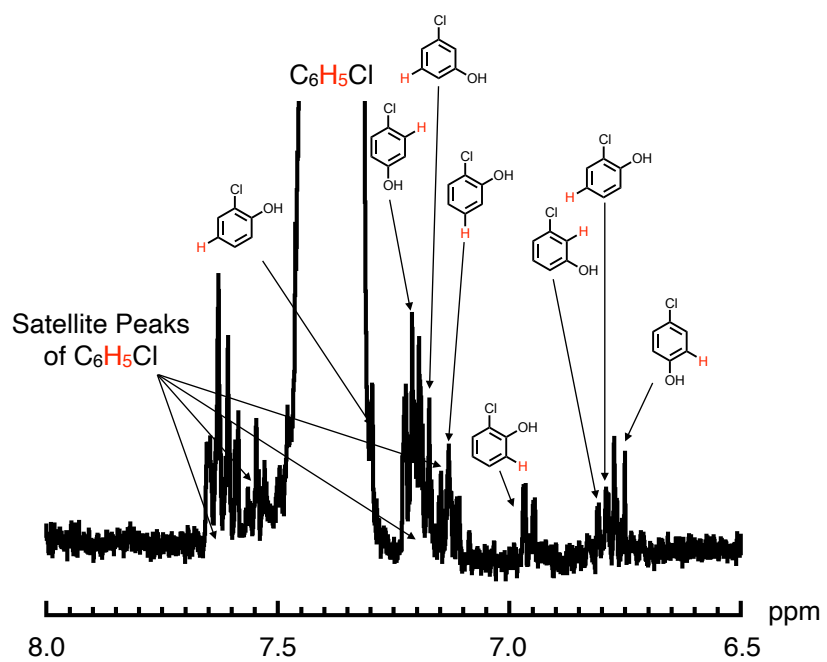


Figure S7. $^1\text{H-NMR}$ spectrum of the reaction mixture of chlorobenzene oxidation by $2^+\text{-I}/\text{SiO}_2$ in a CH_3CN solution containing excess H_2O_2 and TFA at $40\text{ }^\circ\text{C}$ for 6 h.

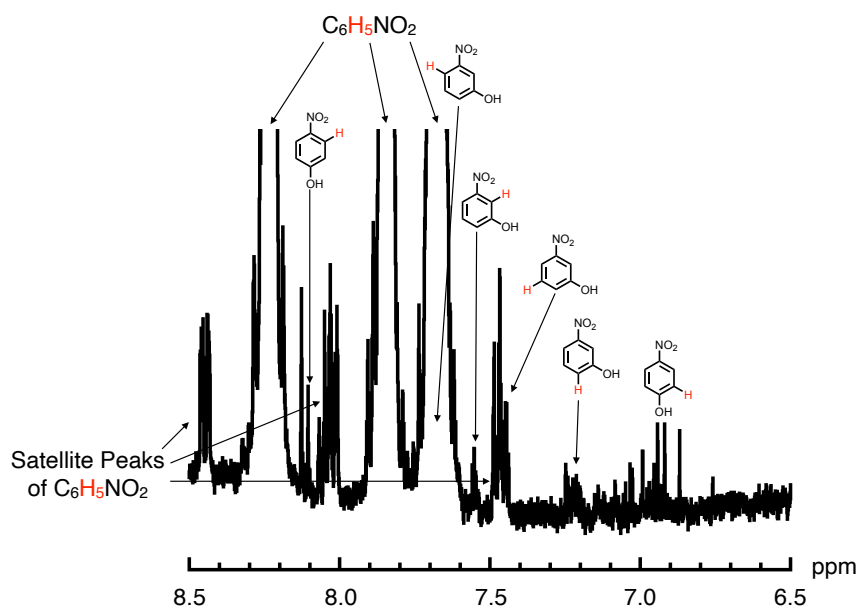


Figure S8. $^1\text{H-NMR}$ spectrum of the reaction mixture of nitrobenzene oxidation by $2^+\cdot\text{I}^-/\text{SiO}_2$ in a CH_3CN solution containing excess H_2O_2 and TFA at 40°C for 6 h.

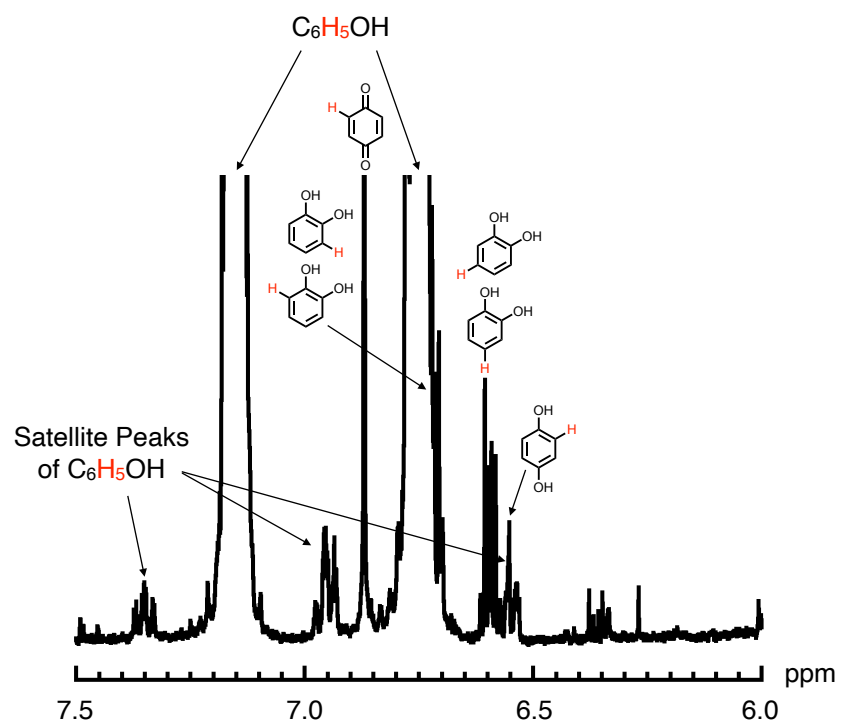


Figure S9. $^1\text{H-NMR}$ spectrum of the reaction mixture of phenol oxidation by $2^+\cdot\text{I}^-/\text{SiO}_2$ in a CH_3CN solution containing excess H_2O_2 and TFA at $40\text{ }^\circ\text{C}$ for 6 h.

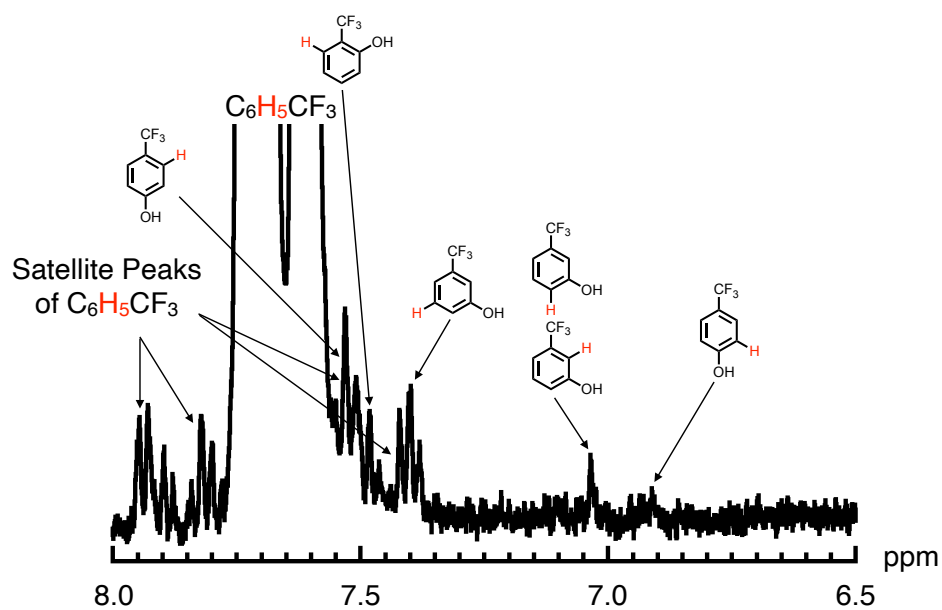


Figure S10. $^1\text{H-NMR}$ spectrum of the reaction mixture of trifluoromethylbenzene oxidation by $2^+\text{I}^-/\text{SiO}_2$ in a CH_3CN solution containing excess H_2O_2 and TFA at $40\text{ }^\circ\text{C}$ for 6 h.

Investigation of the kinetic isotope effects.

Benzene oxidation was performed in a glass tube equipped with magnetic stirrer. A mixture of a solid-supported catalyst (10 mg, 24 μM as $2^+\cdot\text{I}^-$), benzene or benzene- d_6 (470 mM), TFA (24 μL , 138 mM), and 35% aqueous H_2O_2 (100 μL , 514 mM) in CH_3CN (2.0 mL) was heated in an oil bath at 40 $^\circ\text{C}$ with stirring at 900 rpm for 1 h. After the reaction mixture was filtered through a disposable membrane filter (ADVANTEC, DISMIC-13JP), the filtrate (0.10 mL) was diluted with CH_3CN (0.90 mL). The resulting solutions were analysed by GC-MS (Agilent 7890A equipped with JEOL JMS-T100GCV, detection: EI, column: Agilent DB-WAX UI, external standard: 1-chlorodecane (10 μM), temperature conditions: initial: 60 $^\circ\text{C}$ —hold (2 min)—raise to 240 $^\circ\text{C}$ (8 $^\circ\text{C}/\text{min}$)—hold (8 min)).

The retention times of both of $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{D}_5\text{OH}$ were 23.1 min. The concentrations of the corresponding phenols in the reaction mixtures were determined based on the calibration curves for $\text{C}_6\text{H}_5\text{OH}$ or $\text{C}_6\text{D}_5\text{OH}$ as shown below;

C_6H_6 oxidation : $[\text{C}_6\text{H}_5\text{OH}] = 23.1 \mu\text{M}$

C_6D_6 oxidation : $[\text{C}_6\text{D}_5\text{OH}] = 20.3 \mu\text{M}$

Based on these data, $k_{\text{H}}/k_{\text{D}}$ was calculated to be 1.14.

Reference:

- [1] Y. Yamada, J. Kura, Y. Toyoda, K. Tanaka, *Dalton Trans.*, 2021, **50**, 6718–6724.