

Supplementary Information for

**Efficient Catalytic Direct C–H Hydroxylation of Benzene
by Graphite-Supported μ -Nitrido-Bridged
Iron Phthalocyanine Dimer**

Yasuyuki Yamada,^{1,2,*} Yoshiki Uno,¹ Chee–Ming Teoh,¹ Hirotaka Ohkita,² Yuka
Toyoda,² Akiko Sakata,² Yutaka Hitomi,³ and Kentaro Tanaka^{1,4*}

¹*Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku,
Nagoya 464-8602, Japan*

²*Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602,
Japan*

³*Department of Molecular Chemistry and Biochemistry, Graduate School of Science and Engineering,
Doshisha University, Kyotanabe, Kyoto, 610-0321, Japan*

⁴*Research Institute for Quantum and Chemical Innovation, Institutes of Innovation for Future Society,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*

*E-mail: yamada.yasuyuki.i6@f.mail.nagoya-u.ac.jp, kentaro@chem.nagoya-u.ac.jp

Experimental

General

All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. A graphite-supported catalyst (**1**/G) and silica gel-supported catalysts (**3**⁺·I⁻/SiO₂, **1**⁺·I⁻/SiO₂, and **1**/SiO₂) were prepared according to our previous report.^{[1],[2]} ¹H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz for ¹H) or JMN-ECA600 (600 MHz for ¹H) spectrometers at a constant temperature of 298 K.

Benzene oxidation reaction using CH₃CN as a solvent.

Benzene oxidation was performed in a glass tube equipped with a magnetic stirring bar (PTFE). A mixture containing a solid-supported catalyst (10 mg, 49 μM as **1**, **3**⁺·I⁻, or **1**⁺·I⁻), a 500 mM CH₃CN solution of benzene (1.0 mL, initial concentration of benzene in the reaction mixture: 450 mM), TFA (12 μL, 141 mM), and 35% aqueous H₂O₂ (100 μL, initial concentration of H₂O₂ in the reaction mixture: 1.040 M) was stirred by using a magnetic stirrer equipped with an aluminum block-based temperature control module (KPI, Model HHE-19G-US II) at a given temperature 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 40 μL of a standard solution (20 mM 2-(trimethylsilyl)ethanol in DMSO-*d*₆) for quantitative analysis using ¹H-NMR spectroscopy. The singlet peak assignable as the CH₃ moiety of 2-(trimethylsilyl)ethanol was used as the reference for calculating the concentrations of the oxidized products.

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

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

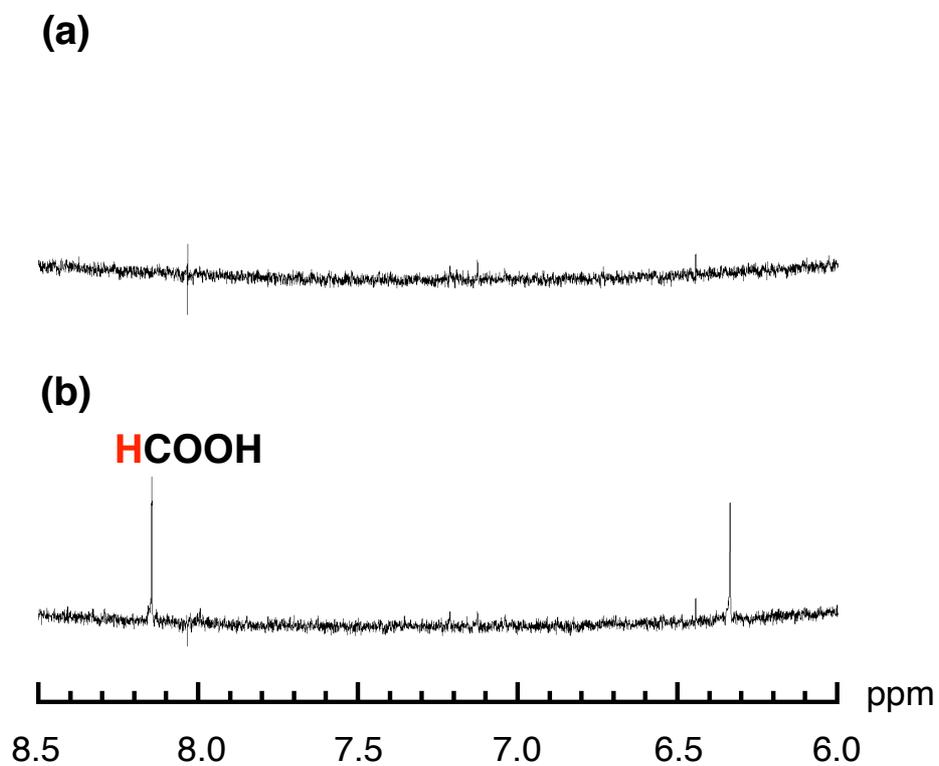


Fig. S1. ^1H -NMR spectrum of the reaction mixtures in the absence of benzene. Mixtures containing CH_3CN (1.0 mL), TFA (12 μL , 141 mM), and 35% aqueous H_2O_2 (100 μL , initial concentration of H_2O_2 was 1.04 M) stirred at 25 $^\circ\text{C}$ for 2 h in the absence (a) and presence (b) of **1**/G (10 mg, 49 μM as **1**).

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

Benzene oxidation in H₂O was performed in a glass tube equipped with a magnetic stirring bar (PTFE). A mixture containing **1/G** (10 mg, 49 μM as **1**), benzene (50 μL, initial concentration of benzene in the reaction mixture: 528 mM), TFA (12 μL, 131 mM), 35% aqueous H₂O₂ (100 μL, initial concentration of H₂O₂ in the reaction mixture: 993 mM), and H₂O (1.0 mL) was stirred at 25 °C for 4 h by using a magnetic stirrer equipped with an aluminum block-based temperature control module (KPI, Model HHE-19G-US II). After the reaction mixture was filtered through a disposable membrane filter (ADVANTEC, DISMIC-13JP), 200 μL of the resulting filtrate was mixed with 340 μL DMSO-*d*₆ and 60 μL of a standard solution (20 mM 2-(trimethylsilyl)ethanol in DMSO-*d*₆) for quantitative analysis using ¹H-NMR spectroscopy.

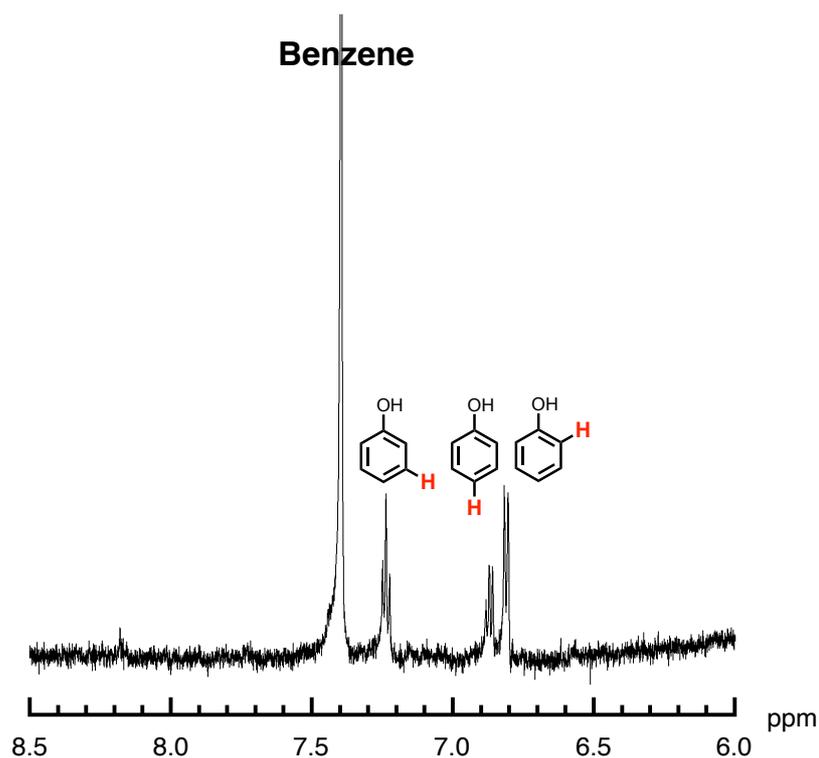


Fig. S2. ¹H-NMR spectrum of the reaction mixtures of benzene oxidation in H₂O at 25 °C for 4 h. The detail of the experiment is summarized above.

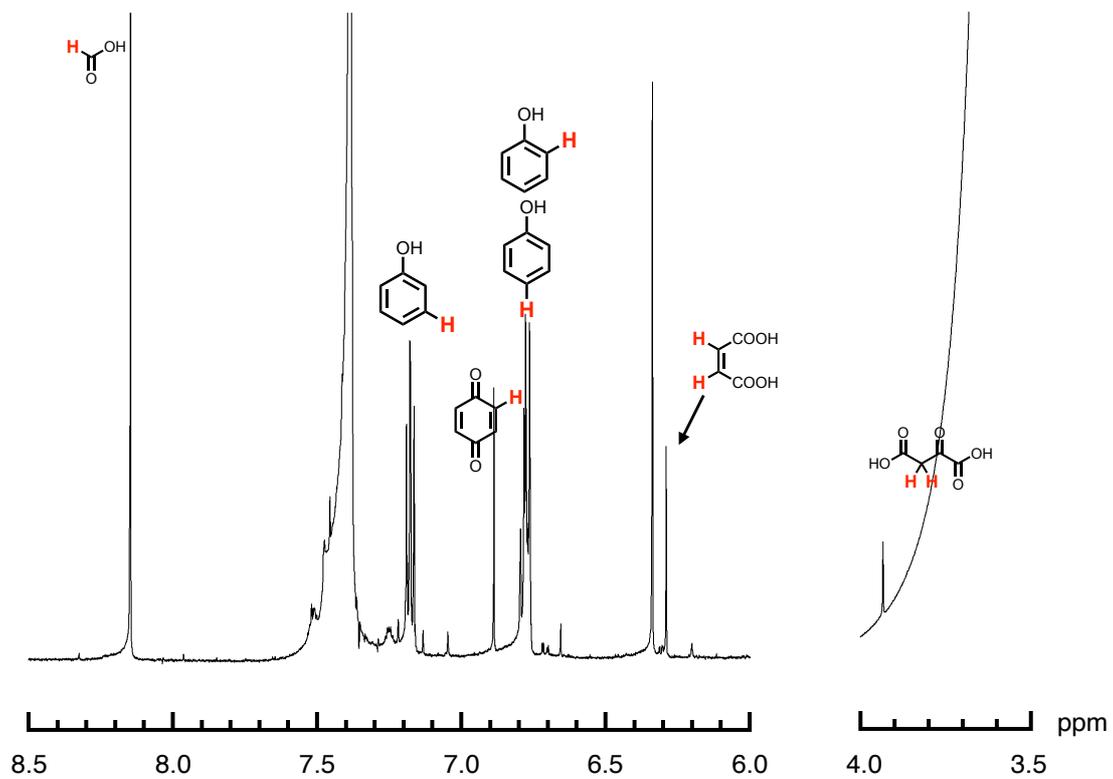


Figure S3. $^1\text{H-NMR}$ spectrum of the reaction mixture of benzene oxidation by 1/G in a CH_3CN solution containing excess H_2O_2 and TFA at $80\text{ }^\circ\text{C}$ for 2 h.

Confirming the stability and reusability of 1/G

In order to check the stability and reusability of 1/G, we compared the benzene oxidation catalytic activity of a used 1/G with that before use.

Benzene oxidation was performed in a vial equipped with a magnetic stirring bar (PTFE). A mixture containing a 1/G (103 mg, 49 μM as **1**), a 500 mM CH_3CN solution of benzene (10 mL, initial concentration of benzene in the reaction mixture: 450 mM), TFA (120 μL , 141 mM), and 35% aqueous H_2O_2 (1.0 mL, initial concentration of H_2O_2 in the reaction mixture: 1.04 M) was stirred at room temperature for 1 h. After the reaction mixture was filtered through a membrane filter (ADVANTEC, PTFE membrane filter (pore size 1.0 μm)), the resulting solid was washed thoroughly with CH_3CN (5 mL \times 3), followed by drying under reduced pressure (1 mmHg) at 60 $^\circ\text{C}$ for 5 h to give the used 1/G (99 mg).

In a similar manner, benzene oxidation was performed by using the used 1/G. A mixture containing the used 1/G (10 mg, 49 μM as **1**), a 500 mM CH_3CN solution of benzene (1.0 mL, initial concentration of benzene in the reaction mixture: 450 mM), TFA (12 μL , 141 mM), and 35% aqueous H_2O_2 (100 μL , initial concentration of H_2O_2 in the reaction mixture: 1.04 M) was stirred at room temperature for 1 h. 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 $\text{DMSO-}d_6$ and 40 μL of a standard solution (20 mM 2-(trimethylsilyl)ethanol in $\text{DMSO-}d_6$) for quantitative analysis using $^1\text{H-NMR}$ spectroscopy. The singlet peak assignable as the CH_3 moiety of 2-(trimethylsilyl)ethanol was used as the reference for calculating the concentrations of the oxidized products.

• unused 1/G ;

[phenol] = 14.7 ± 0.5 mM, [*p*-quinone] = 0.6 ± 0.1 mM, TON_{BC} (2 h) = 310 ± 13

• used 1/G;

[phenol] = 14.5 ± 0.3 mM, [*p*-quinone] = n.d., TON_{BC} (2 h) = 293 ± 5

Oxidation of benzene derivatives

Summary of the oxidation reactions of benzene derivatives by **1/G** at 25 °C for 2 h is shown in Table 2 in the main text. In the case of benzene oxidation, almost linear increase in the BCN was observed up to 2 h. Turn over numbers of benzene derivatives (TONs) were calculated from the total concentration of the oxidized products obtained from the results of ¹H-NMR measurements. The ¹H-NMR spectra used for quantitative analyses of the oxidized compounds are shown in Figures S4–S7.

Initial reaction conditions: **1/G** (10 mg, 49 μM as **1**), a 500 mM CH₃CN solution of a benzene derivative (bromobenzene, chlorobenzene, trifluoromethylbenzene, or nitrobenzene) (1.0 mL, initial concentration of a benzene derivative in the reaction mixture: 450 mM), TFA (12 μL, 141 mM), and 35% aqueous H₂O₂ (100 μL, initial concentration of H₂O₂ in the reaction mixture: 1.040 M).

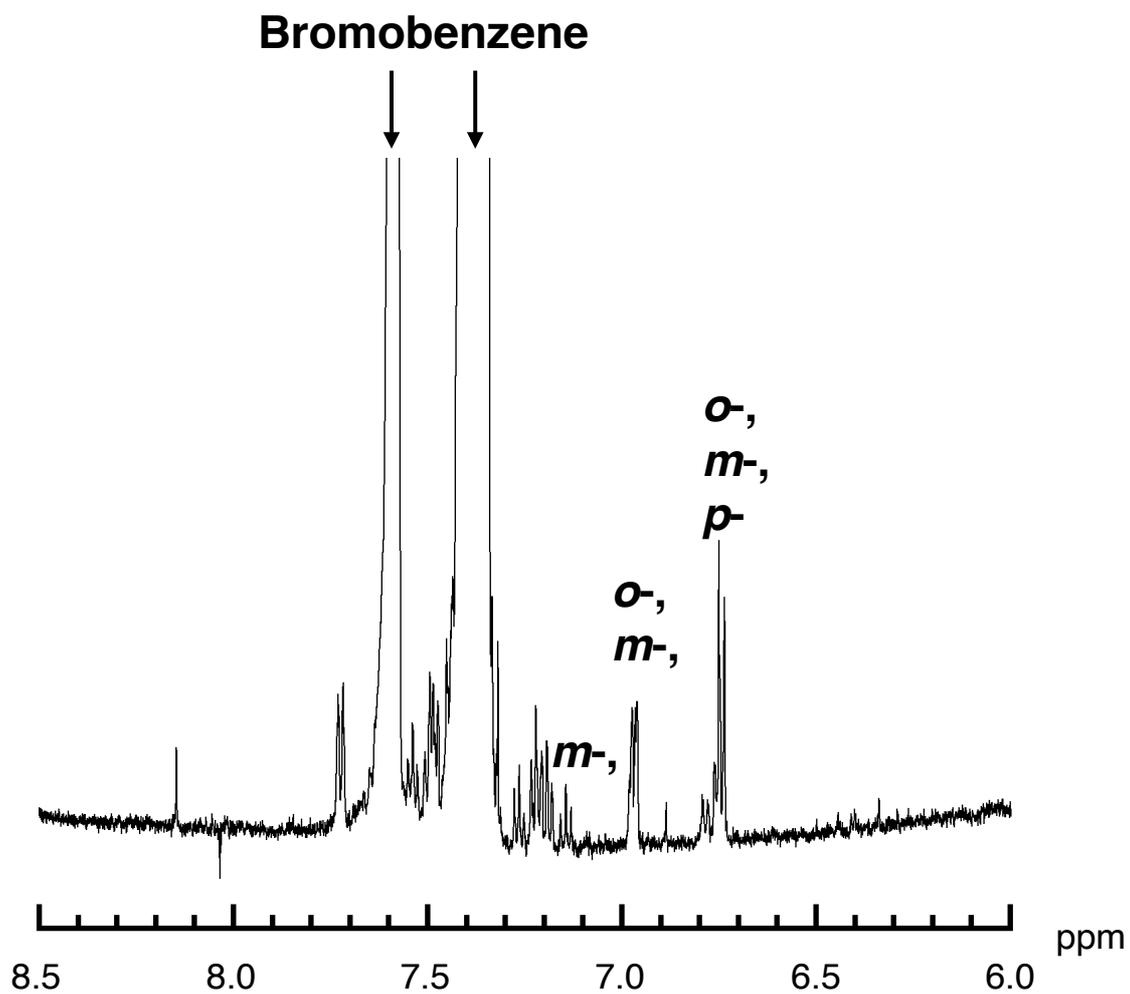


Figure S4. ¹H-NMR spectrum of the reaction mixture of bromobenzene oxidation by 1/G in a CH₃CN solution containing excess H₂O₂ and TFA at 25 °C for 2 h.

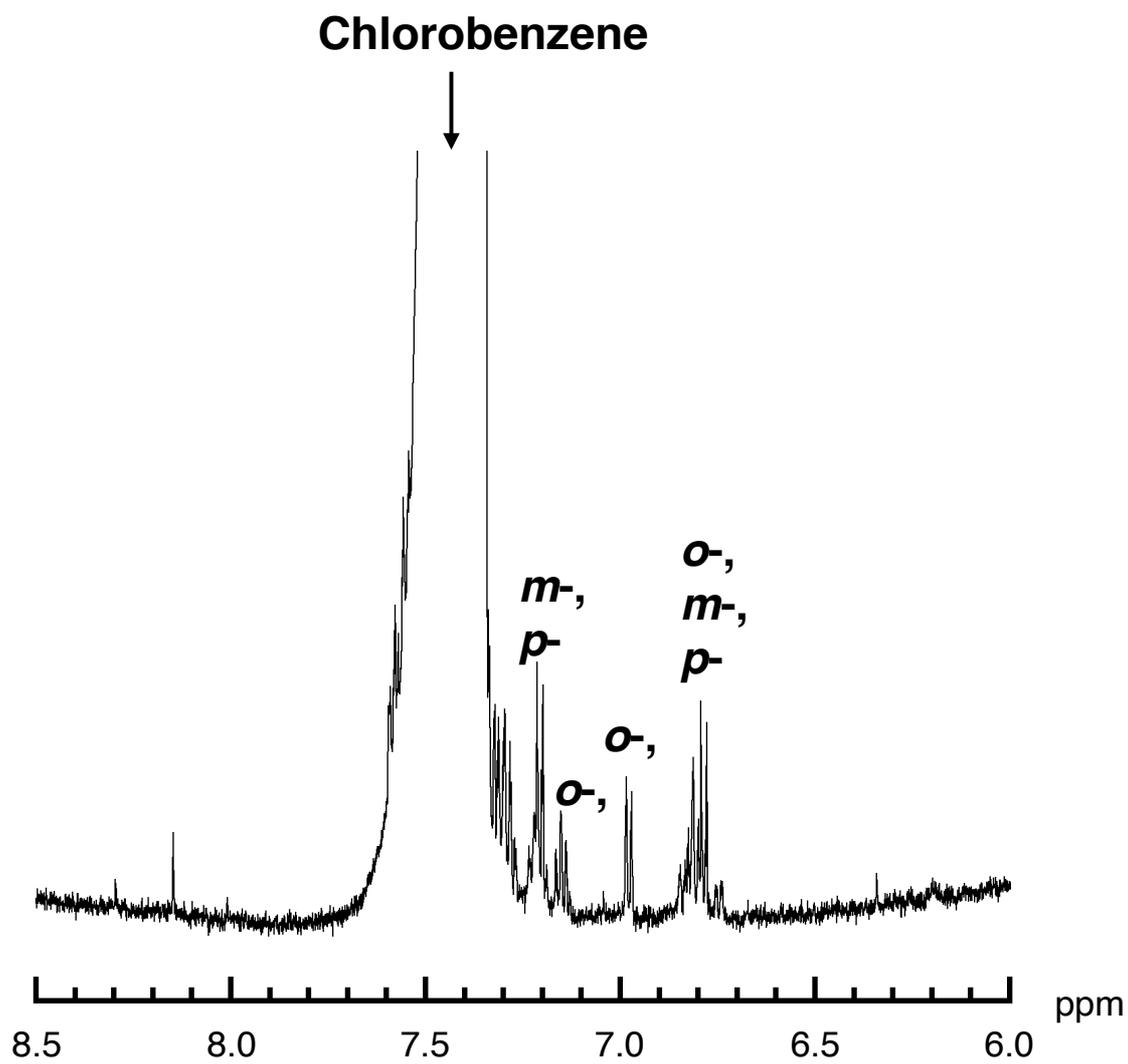


Figure S5. ^1H -NMR spectrum of the reaction mixture of chlorobenzene oxidation by **1/G** in a CH_3CN solution containing excess H_2O_2 and TFA at $25\text{ }^\circ\text{C}$ for 2 h.

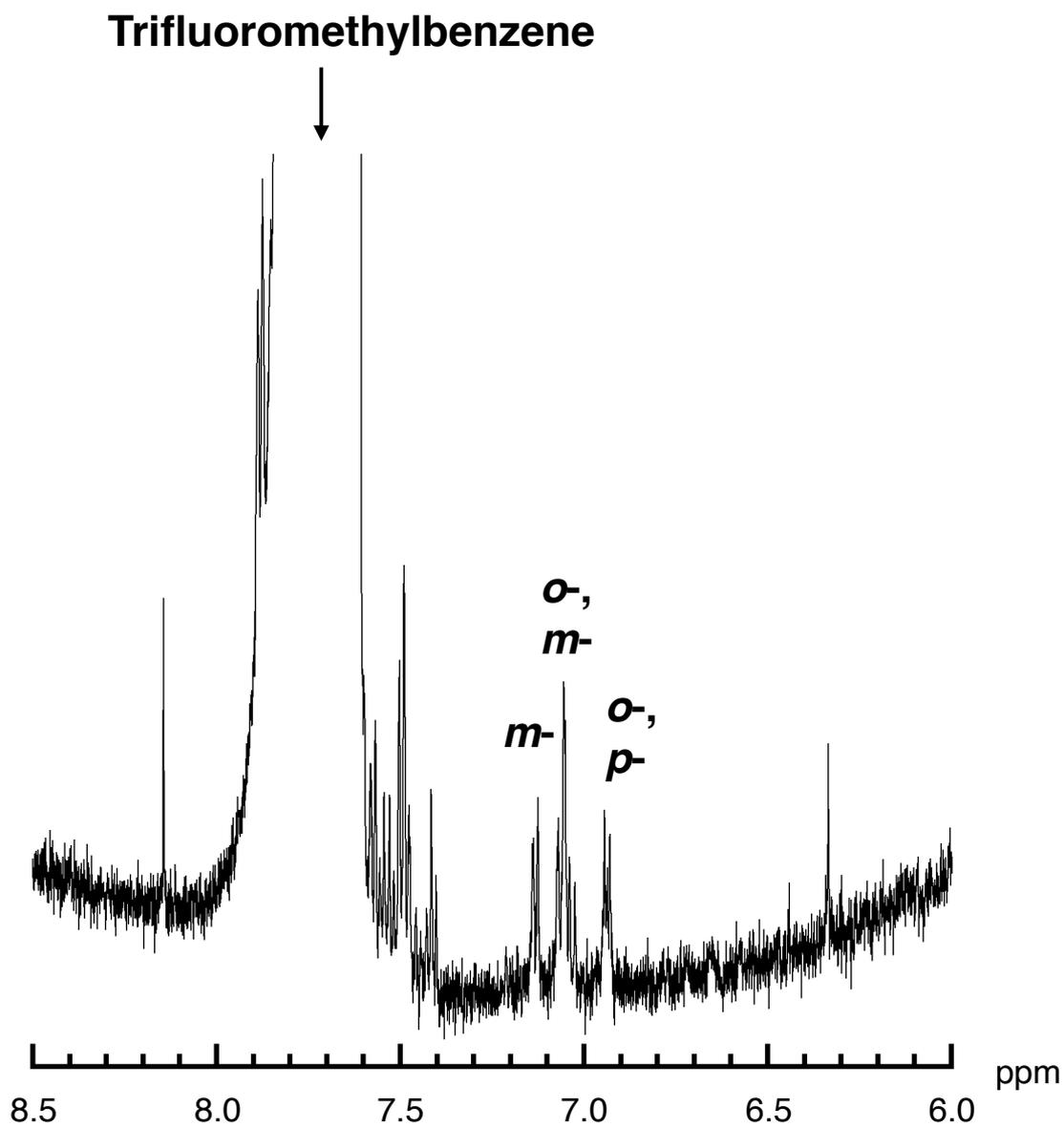


Figure S6. ^1H -NMR spectrum of the reaction mixture of trifluoromethylbenzene oxidation by **1/G** in a CH_3CN solution containing excess H_2O_2 and TFA at 25 °C for 2 h.

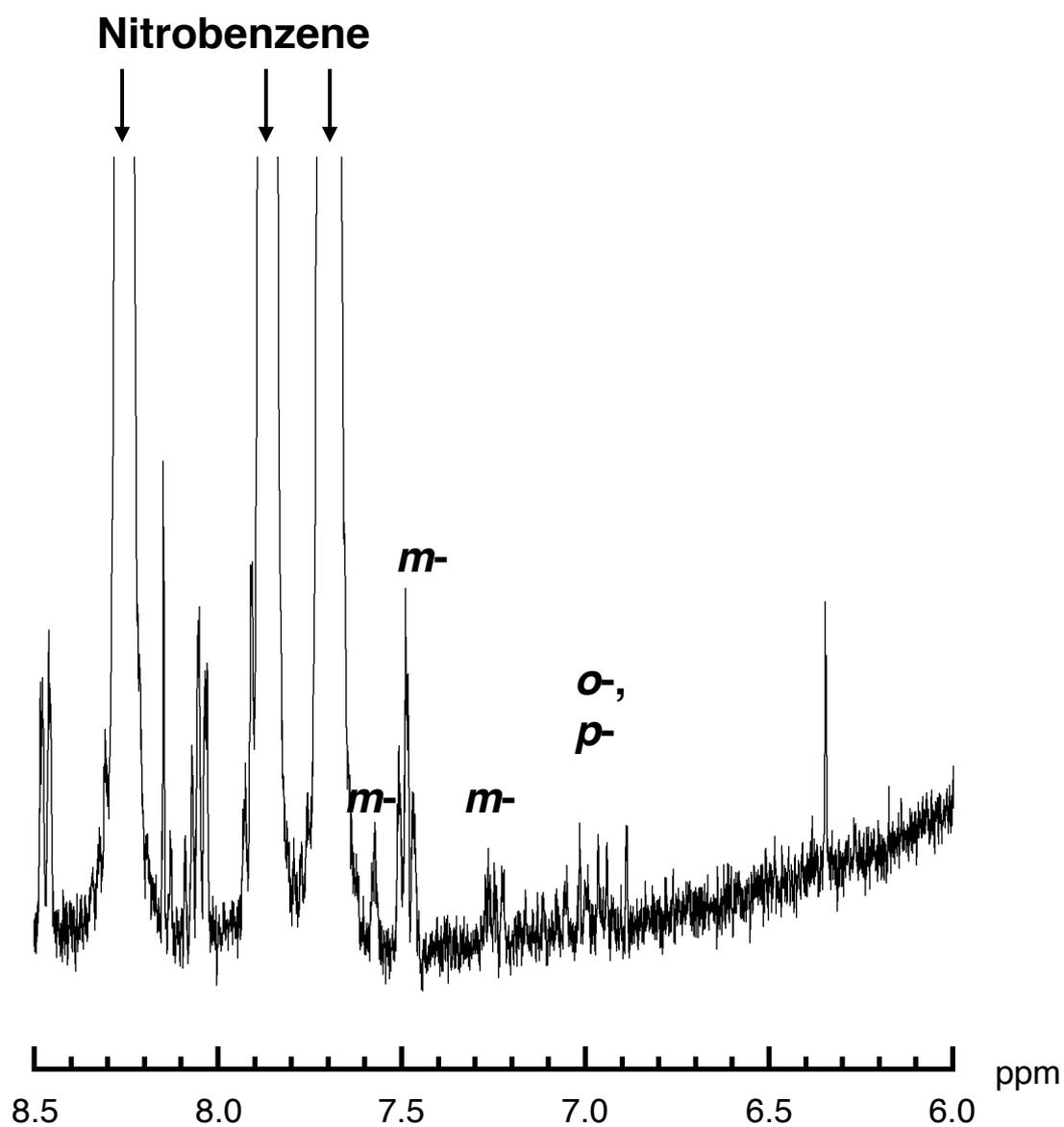


Figure S7. ^1H -NMR spectrum of the reaction mixture of chlorobenzene oxidation by 1/G in a CH_3CN solution containing excess H_2O_2 and TFA at 25 °C for 2 h.

Investigation of the kinetic isotope effects.

Benzene or benzene- d_6 oxidation was performed in a glass tube equipped with a magnetic stirring bar (PTFE). A mixture containing 1/G (10 mg, 49 μM as **1**), 500 mM benzene in CH_3CN (1.0 mL, initial concentration of benzene or benzene- d_6 : 450 mM), TFA (12 μL , 141 mM), and 35% aqueous H_2O_2 (100 μL , initial concentration of H_2O_2 : 1.040 M) was stirred by using a magnetic stirrer equipped with an aluminum block-based temperature control module (KPI, Model HHE-19G-US II) at 25 $^\circ\text{C}$ 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 22.9 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 $\text{C}_6\text{D}_5\text{OH}$. Determination experiments of the KIE value for the benzene oxidation by 1/G were repeated by 4 times to obtain the $k_{\text{H}}/k_{\text{D}}$ values of 0.78, 1.28, 0.91, and 1.01.

Based on the average of the $k_{\text{H}}/k_{\text{D}}$ values obtained above, KIE value was determined to be 1.0.

Reference:

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

[2] Y. Yamada, K. Morita, T. Sugiura, Y. Toyoda, N. Mihara, M. Nagasaka, H. Takaya, K. Tanaka, T. Koitaya, N. Nakatani, H. Ariga-Miwa, S. Takakusagi, Y. Hitomi, T. Kudo, Y. Tsuji, K. Yoshizawa, K. Tanaka, *JACS Au*, 2023, **3**, 823–833.