Electronic Supplementary Information

One-Step Selective Hydroxylation of Benzene to Phenol with Hydrogen Peroxide Catalysed by Copper Complexes Incorporated into Mesoporous Silica- Alumina

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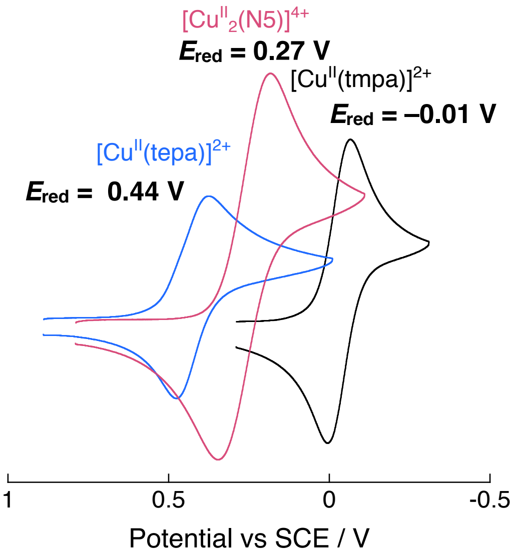

Figure S1. Cyclic voltammogram of $[Cu^{II}(tmpa)(CH_3CN)](ClO_4)_2$ (1.0 mM), $[Cu^{II}_2(N5)(H_2O)_2](NO_3)_4$ (1.0 mM), and $[Cu^{II}(tepa)(ClO_4)](ClO_4)$ (1.0 mM) in deaerated CH_3CN containing n-Bu_4NPF_6 (0.10 M) with a platinum disk electrode (i.d. 1.6 mm) at 298 K. Scan rate: 100 mV s^{-1}.

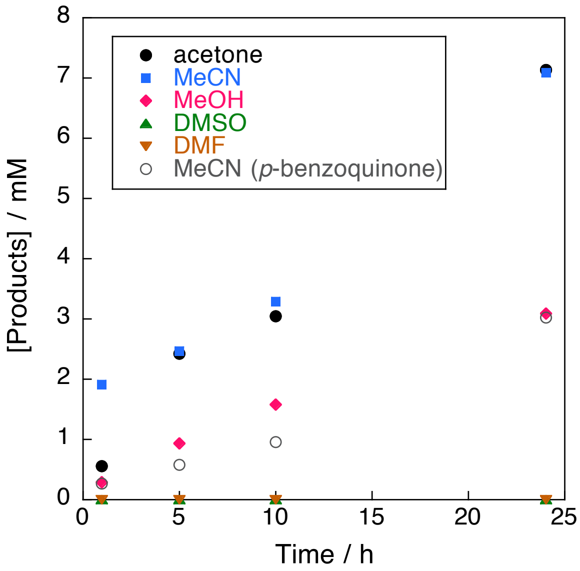

Figure S2. Time profiles of formation of phenol or *p*-benzoquinone in the hydroxylation of benzene with 30 wt% aqueous H_2O_2 and a catalytic amount of **1** at 298 K in various solvents (4.75 ml). Symbols correspond as follows: Solid circle, acetone; solid square, acetonitrile; pink diamond, MeOH; green triangle, DMSO; orange inverted triangle, DMF; grey open circle, acetonitrile (*p*-benzoquinone). The concentrations are $[C_6H_6]$ = 2.1 M, $[H_2O_2]$ = 2.1 M and $[[Cu^{II}(tmpa)]^{2+}]$ = 67 μM in 4.75 ml of the starting solutions.

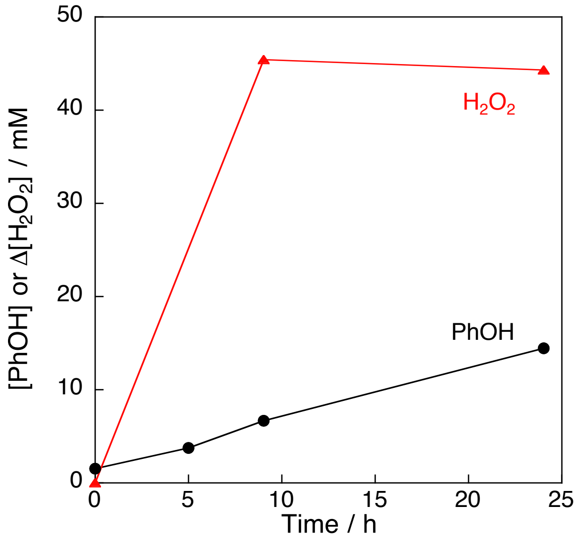

Figure S3. Time profiles of formation of phenol (black circle) and consumption of H_2O_2 (red triangle) in the hydroxylation of benzene with 30 wt% aqueous H_2O_2 with a Cu(II) complex catalyst **1** in acetone at 298 K. The concentrations are $[C_6H_6]$ = 2.1 M, $[H_2O_2]$ = 0.6 M and $[[Cu^{II}(tmpa)]^{2+}]$ = 200 μM in 4.75 ml of the starting solution.

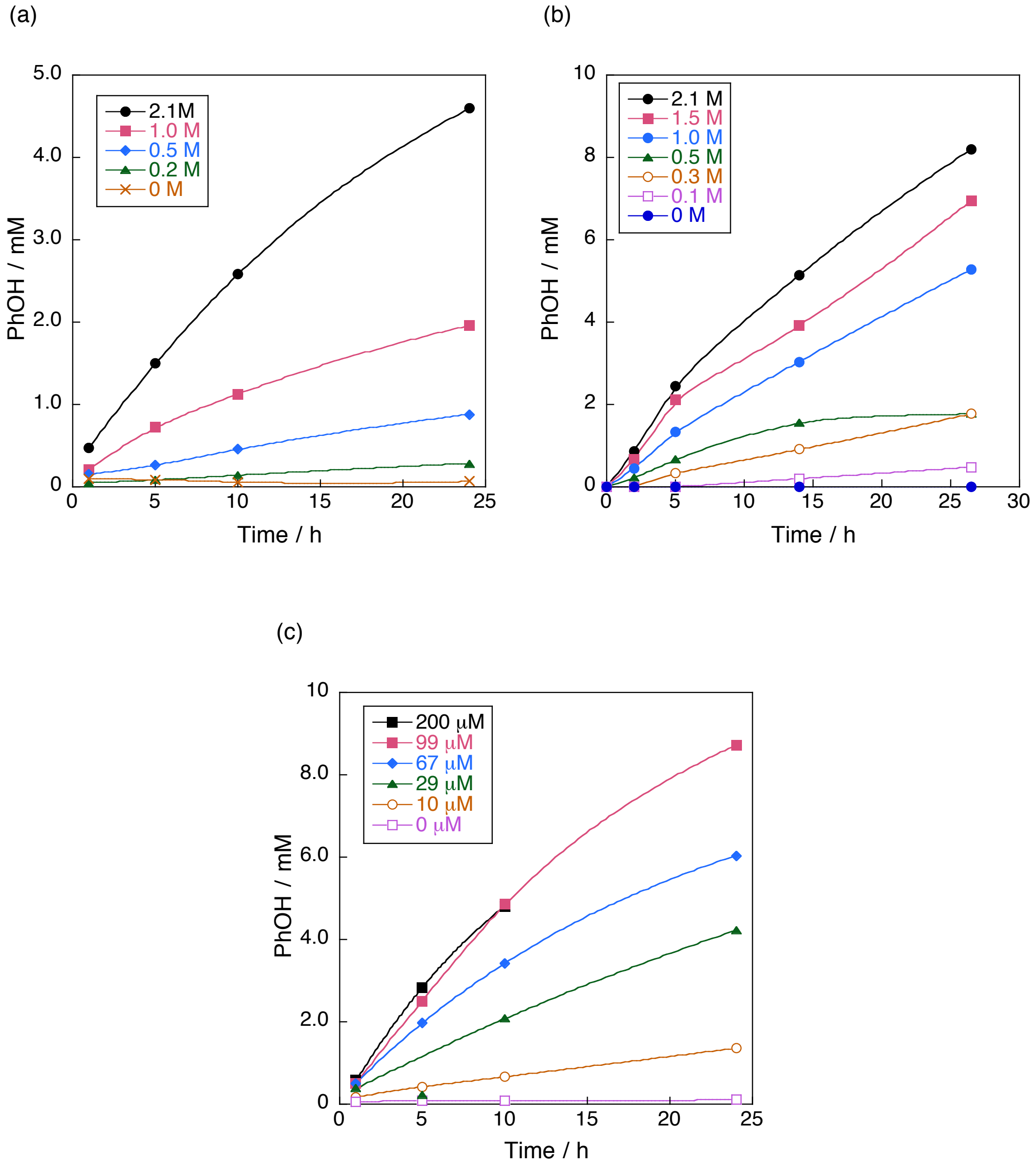

Figure S4. Time profiles of formation of phenol in the hydroxylation of benzene (a) with various amounts of H_2O_2 (0, 0.2, 0.5, 1.0, 2.1 M) with **1** and 1.0 M C_6H_6, (b) from various amounts of benzene (0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.1 M) with H_2O_2 and with **1**, and (c) with various amounts of **1** (0, 10, 29, 67, 99, 200 μM) The concentrations are $[C_6H_6]$ = 2.1 M, $[H_2O_2]$ = 2.1 M, $[H_2O]$ = 8.4 M and $[[Cu^{II}(tmpa)]^{2+}]$ = 67 μM in acetone (4.75 ml) at 298 K unless otherwise noted.

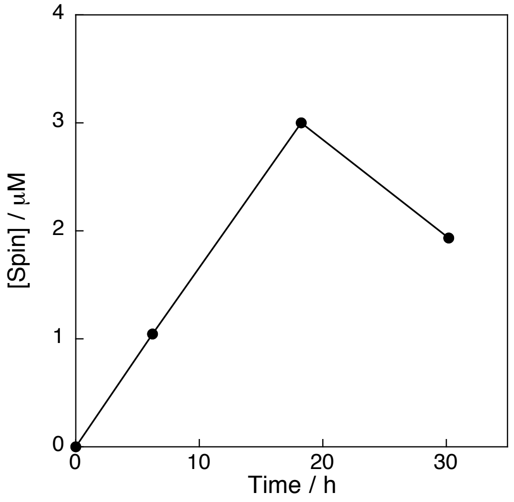

Figure S5. Time profiles of the spin concentration determined by comparing with a reference 2,2-diphenyl-1-picrylhydrazyl radical produced in an acetone solution of benzene, 30 wt% aqueous H_2O_2 and **1** with DMPO at 298 K. The concentrations are $[C_6H_6] = 2.1$ M, $[H_2O_2] = 2.1$ M, $[H_2O] = 0.4$ M, $[[Cu^{II}(tmpa)]^{2+}] = 67$ μM and $[DMPO] = 5.4$ mM in acetone (4.75 ml).

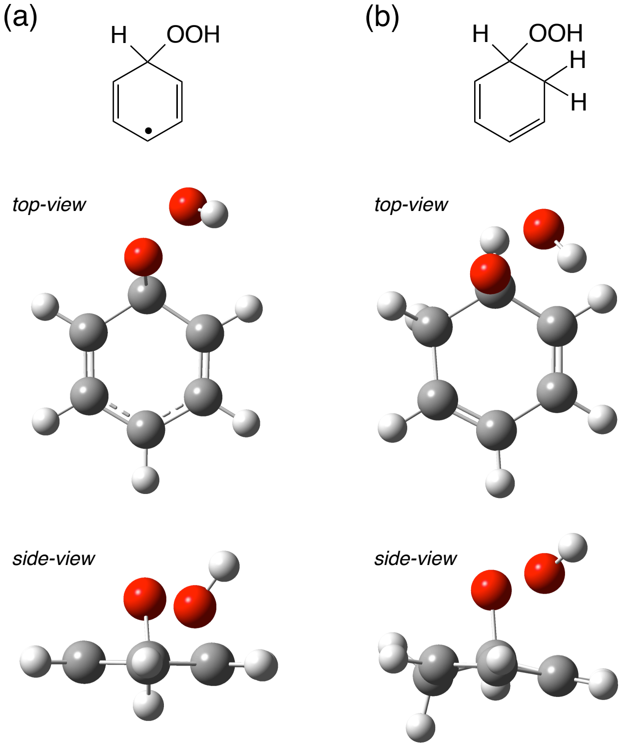

Figure S6. Structural formulas and optimised structures of (a) an OOH-adduct radical and (b) hydrogen-transferred OOH-adduct transition state calculated by a DFT method at the B3LYP/6-31++G(d) level.

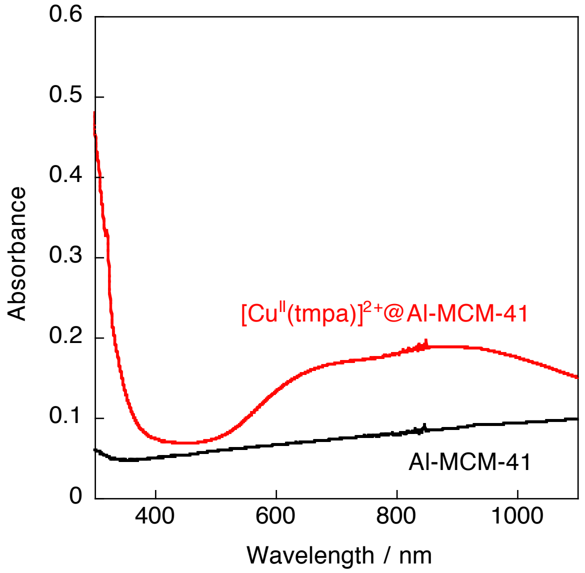

Figure S7. UV-vis diffuse reflectance spectra of $[Cu(tmpa)]^{2+}$@Al-MCM-41 (red line) and Al-MCM-41 (black line)

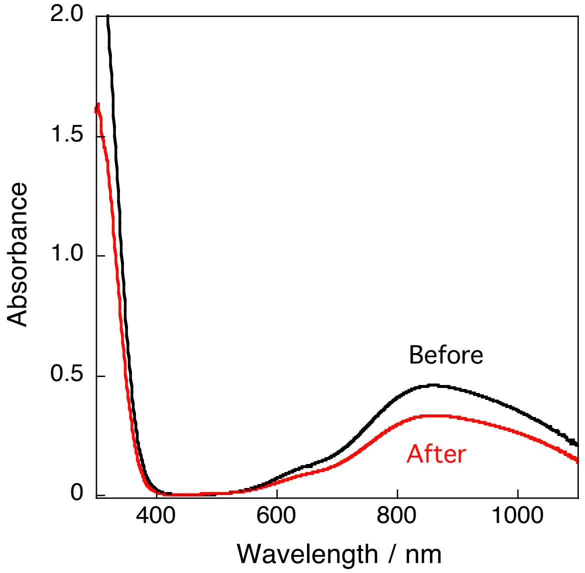

Figure S8. UV-vis absorption spectra of the mother liquid containing $[Cu(tmpa)]^{2+}$ before and after stirring with Al-MCM-41 (300 mg) in acetonitrile at 298 K. The initial conditions are $[[Cu(tmpa)]^{2+}]$ = 1.85 mM in acetonitrile (15 ml) at 298 K.

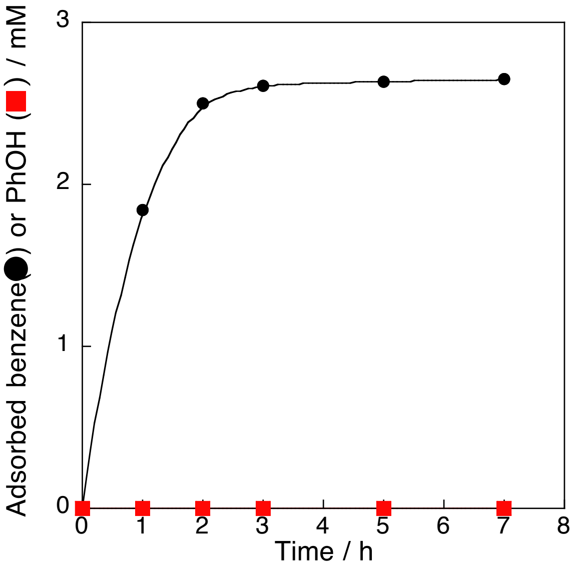

Figure S9. Adsorbed benzene and PhOH by Al-MCM-41 (100 mg) in 4.75 ml of an aqueous solution of benzene (5.1 mM) and PhOH (5.0 mM).

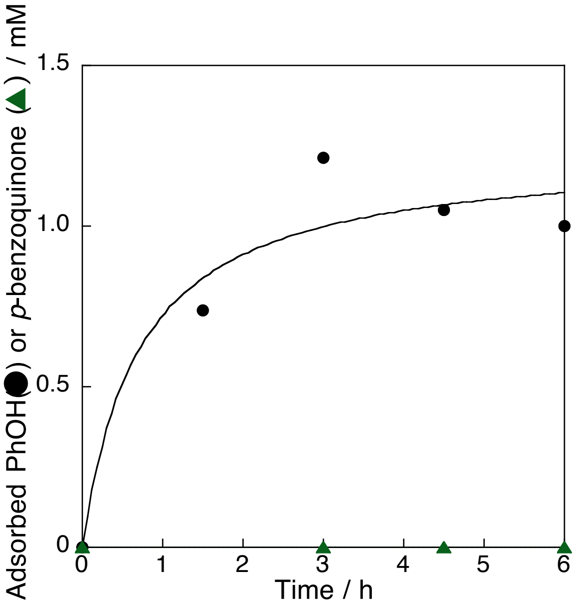

Figure S10. Adsorbed benzene by Al-MCM-41 (50 mg) in 5.0 ml of an acetone/H_2O 4:1 mixed solution of benzene (5.0 mM), and adsorbed PhOH by Al-MCM-41 (50 mg) in 5.0 ml of an acetone/H_2O 4:1 mixed solution of PhOH (5.0 mM). The concentration is $[H_2O] = 8.4$ M is the same as found in the reaction conditions.

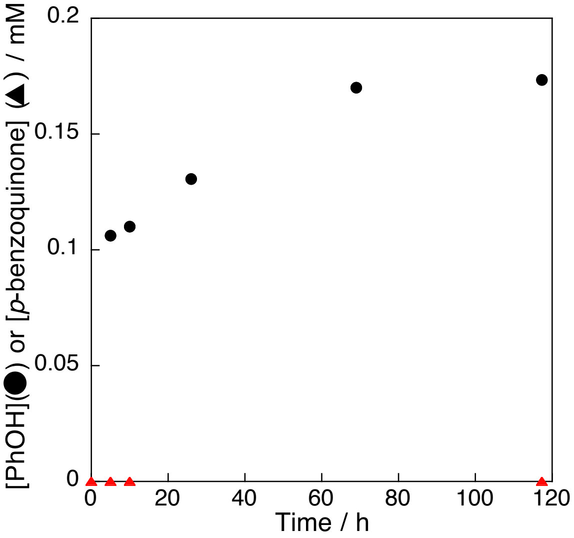

Figure S11. Time profiles of formation of phenol (black solid circle) and *p*-benzoquinone (red solid triangle) in the hydroxylation of benzene with 30 wt% aqueous H_2O_2 and $[Cu^{II}(tmpa)]^{2+}$@Al-MCM-41 at 298 K in acetone (4.75 ml). The concentrations are $[C_6H_6]$ = 1.0 mM, $[H_2O_2]$ = 2.1 M and $[[Cu^{II}(tmpa)]^{2+}]$ = 200 μM.

Table S1. Energy of compounds calculated by DFT method at the B3LYP/6-31++G(d) level.

Compounds	Energy (au)	Compounds	Energy (au)
1	–150.9105	5	–383.7789
2	–232.2590	6	–76.4227
3	–383.1519	7	–307.4805
4	–151.5465		

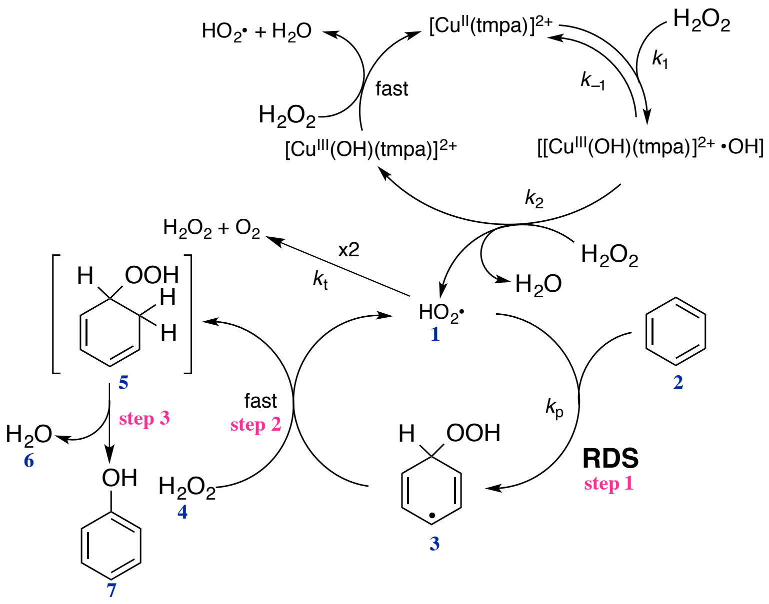

Table S2. Stabilisation energy of each step calculated from results of DFT calculations (1 au = 627.509 kcal mol^{-1}).

Step	Initial state (kcal mol^{-1})	Final state (kcal mol^{-1})	Stabilisation energy (kcal mol^{-1})
1	–240442.5	–240431.4	–11.1
2	–335528.3	–335522.7	–5.6
3	–240824.92	–240902.9	77.9