

## Supporting Information

### Chemo-selectivity of IBX oxidation of hydroxybenzyl alcohols in the presence of Hemicucurbit[6]uril

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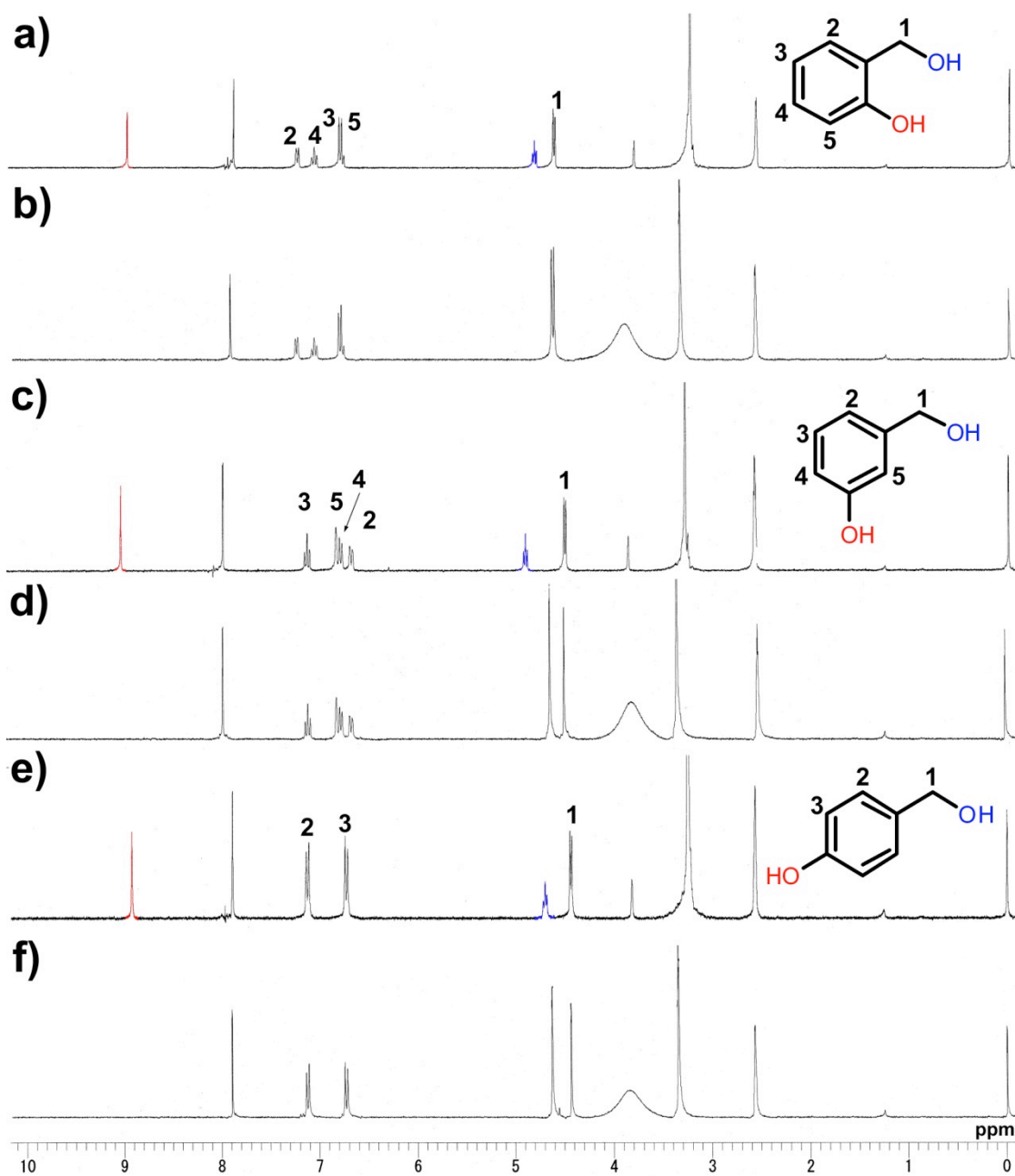
P3 – **Figure S2.** IR analysis of the host-guest interactions between hydroxybenzyl alcohols and HemiQ[6].

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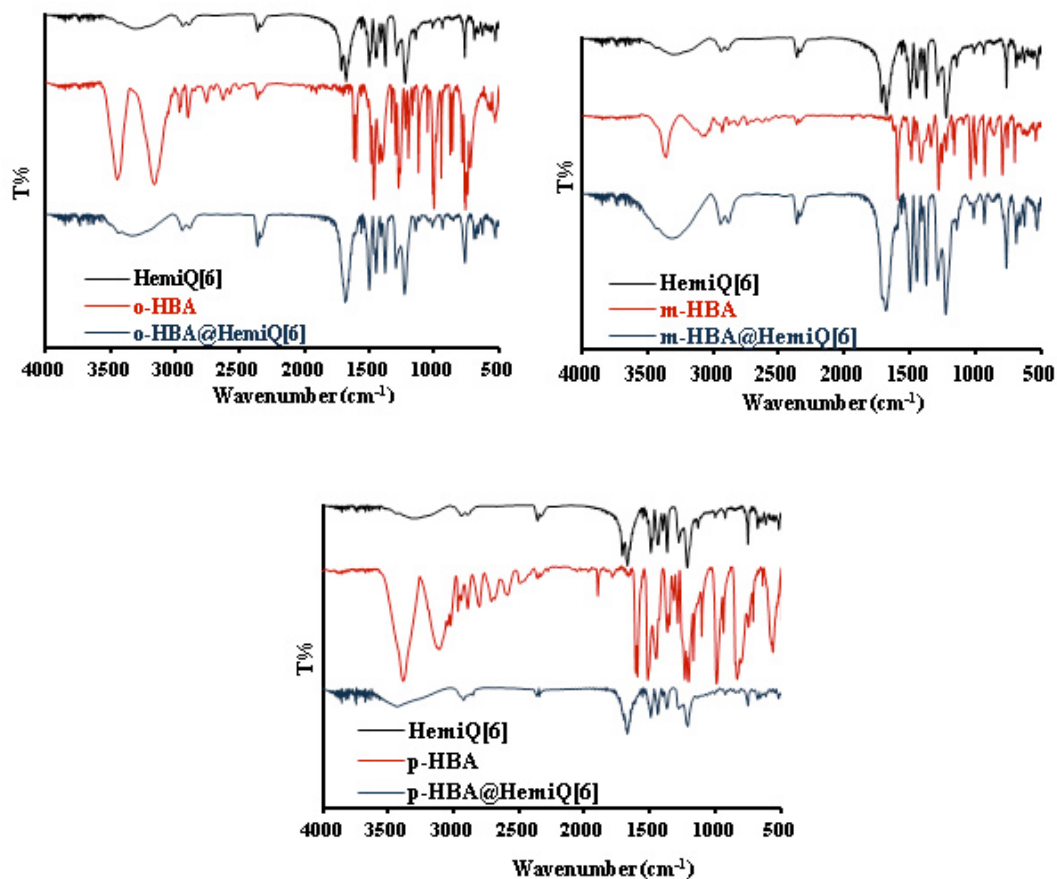
P6 – **Figure S5.** <sup>1</sup>H NMR spectra of *o*-quinone products.

P7 – **Figure S6.** <sup>1</sup>H NMR Spectra of IBX oxidizing hydroxybenzyl alcohols in the absence of HemiQ[6].



**Figure S1** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub>, 2:1, v/v) of a) 2-hydroxybenzyl alcohol; b) 2-hydroxybenzyl alcohol in the presence of HemiQ[6] in a ratio of 1 : 1; c) 3-hydroxybenzyl alcohol; d) 3-hydroxybenzyl alcohol in the presence of HemiQ[6] in a ratio of 1 : 1; e) 4-hydroxybenzyl alcohol; f) 4-hydroxybenzyl alcohol in the presence of HemiQ[6] in a ratio of 1 : 1.

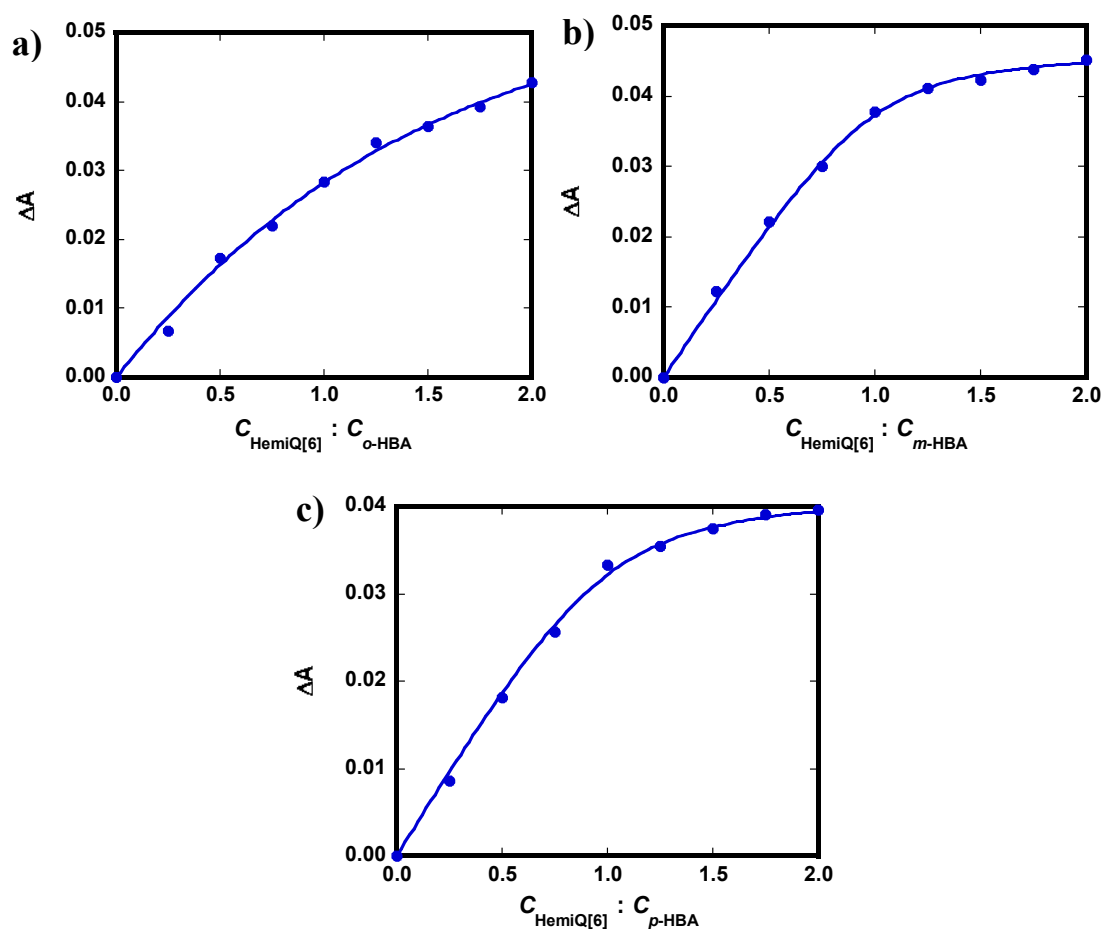
All of active protons of hydroxybenzyl alcohols were fading away after addition of HemiQ[6], and the broad peaks have been observed, which confirm that the form of hydrogen bondings between hydroxybenzyl alcohols and HemiQ[6].



**Figure S2** IR spectra of HemiQ[6], a) 2-hydroxybenzyl alcohol; b) 3-hydroxybenzyl alcohol; c) 4-hydroxybenzyl alcohol, and the corresponding inclusion complexes.

IR spectra were recorded on a JASCO FT-IR 4200A spectrophotometer using KBr pellets. Each inclusion complex was prepared by stirring the mixture solution of HemiQ[6] with corresponding guest in CHCl<sub>3</sub> in a ratio of 1:1 at 60°C, and then the solvent was removed in vacuum to get the solid inclusion complexes.

Both the bands at 1714 and 1678 cm<sup>-1</sup> were attributed to the carbonyl stretching vibration in free HemiQ[6], and the IR band at 1710 cm<sup>-1</sup> in the spectrum of inclusion complex confirmed the host-guest interactions, which have been attributed to  $\nu_{C=O}$  of bound HemiQ[6].



**Figure S3** Non-linear fitting of UV-vis titrations of a) *o*-hydroxybenzyl alcohol; b) *m*-hydroxybenzyl alcohol; c) *p*-hydroxybenzyl alcohol with HemiQ[6].

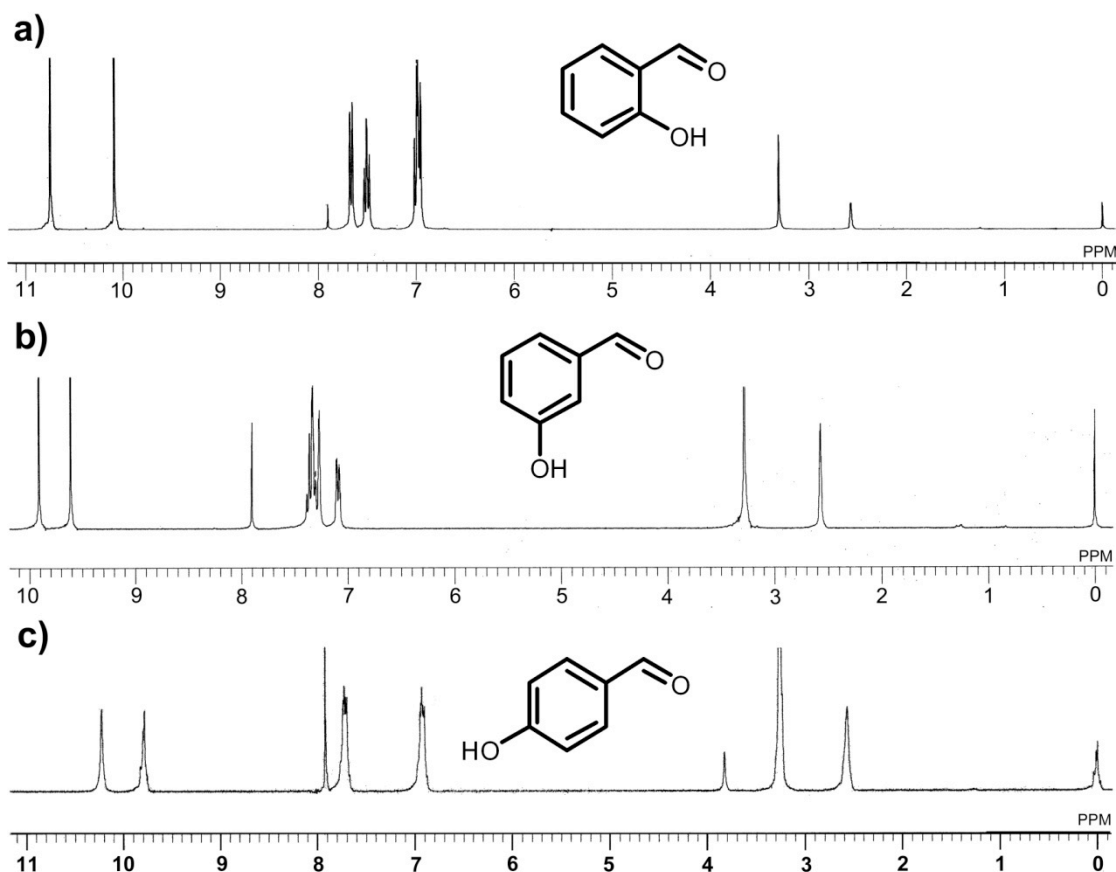
For the host-guest interaction in a ratio of 1 : 1, the equilibrium of H (Host), G (Guest) and H·G (inclusion complex) is expressed by eq (1):



The corresponding association constant ( $K_a$ ) could be obtained by non-linear least square fitting according to eq (2)

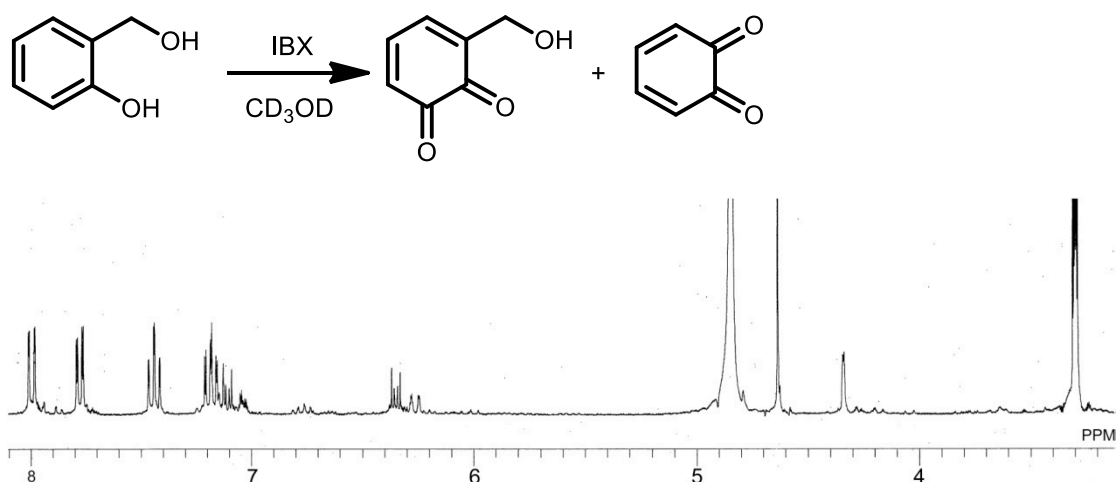
$$\Delta A = \frac{\Delta \varepsilon ([\text{H}]_0 + [\text{G}]_0 + 1/K_a) \pm \sqrt{\Delta \varepsilon^2 ([\text{H}]_0 + [\text{G}]_0 + 1/K_a)^2 - 4\Delta \varepsilon^2 [\text{H}]_0 [\text{G}]_0}}{2} \quad (2)$$

where  $\Delta A$  is the change in the absorbance of guest on gradual addition of TMeQ[6], whereas  $\Delta \varepsilon$  refers to the difference of molar absorptivity between complexed and free G; the total concentration of host and guest is denoted by  $[\text{H}]_0$  and  $[\text{G}]_0$ . Accordingly, the association constants of the interaction between HemiQ[6] and 2,3,4-hydroxybenzyl alcohols are  $(4.8 \pm 1.5) \times 10^3 \text{ L}\cdot\text{mol}^{-1}$ ,  $(7.4 \pm 2.2) \times 10^4 \text{ L}\cdot\text{mol}^{-1}$  and  $(5.5 \pm 1.6) \times 10^4 \text{ L}\cdot\text{mol}^{-1}$ , respectively.

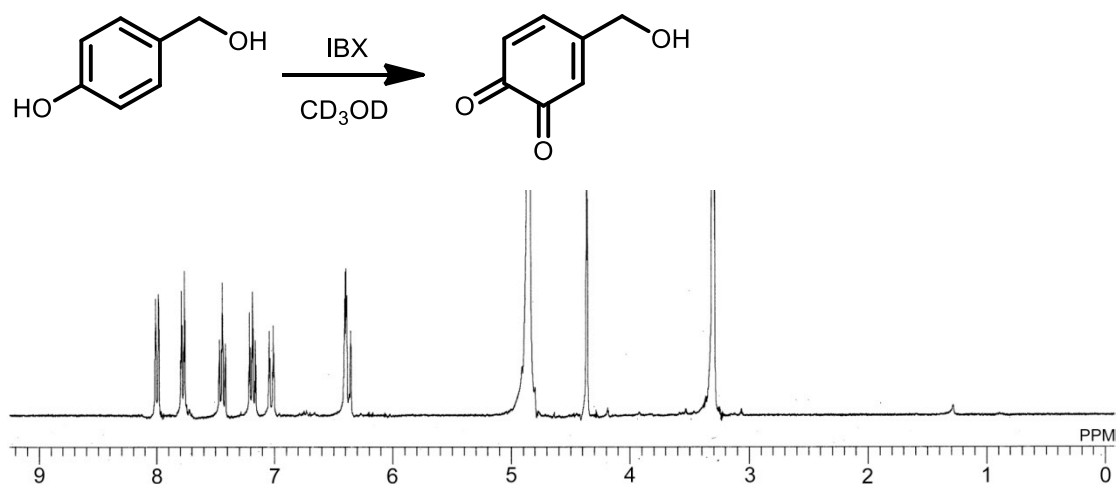


**Figure S4**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{DMSO}-d_6$ , 2:1, v/v, 300 MHz, 25 °C) spectra of a) 2-hydroxybenzaldehyde; b) 3-hydroxybenzaldehyde; c) 4-hydroxybenzaldehyde.

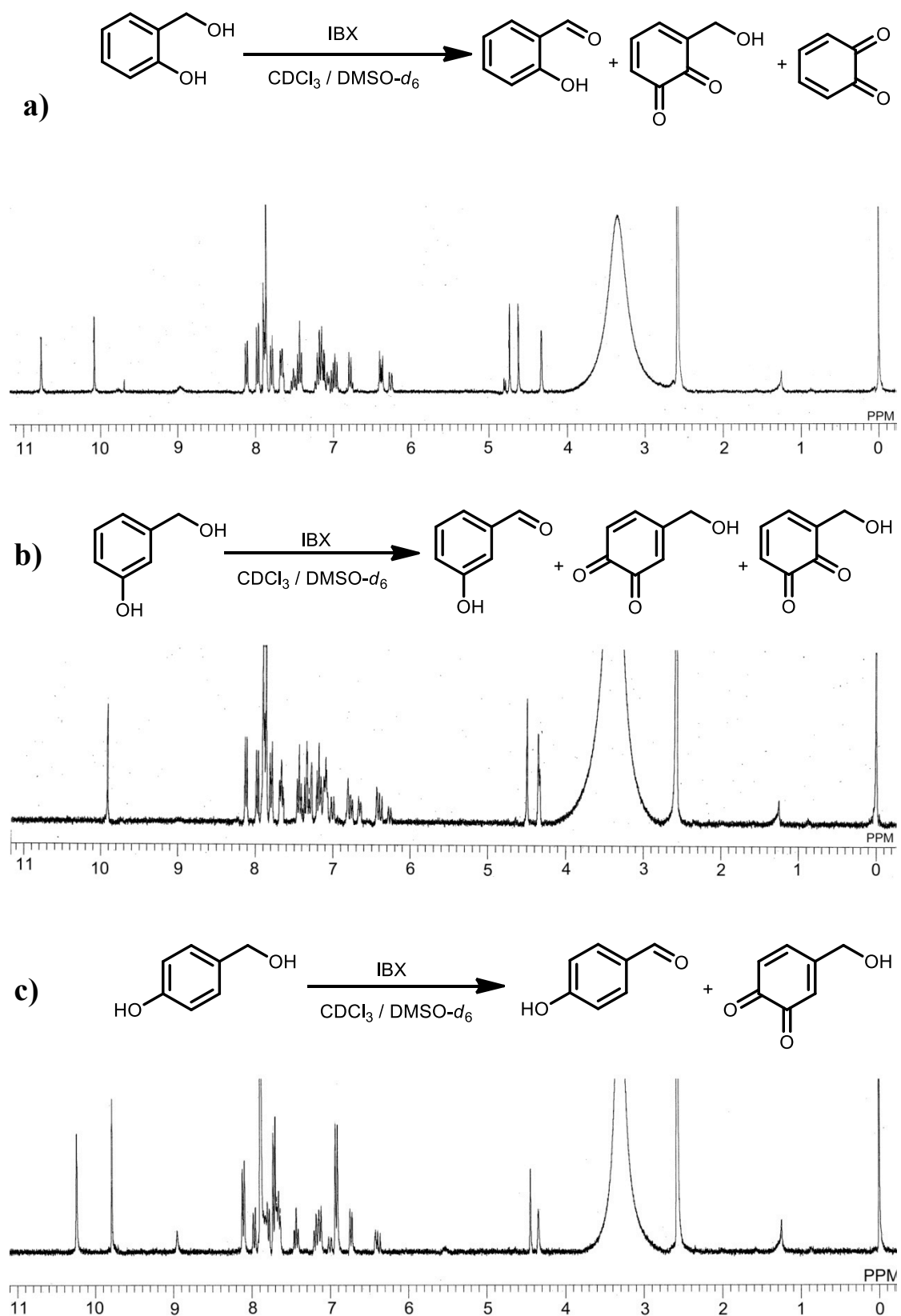
To confirm the aldehyde products of IBX oxidation of hydroxybenzyl alcohols,  $^1\text{H}$  NMR spectra of the standard samples of hydroxyl benzylaldehydes have been measured. *o*-Hydroxybenzaldehyde:  $^1\text{H}$  NMR  $\delta$  6.98 ppm (m, 2H),  $\delta$  7.50 ppm (t, 1H,  $J = 7.8$ ),  $\delta$  7.66 ppm (d, 2H,  $J = 7.8$ ),  $\delta$  10.1 ppm (s, 1H),  $\delta$  10.7 ppm (s, 1H). *m*-Hydroxybenzaldehyde:  $^1\text{H}$  NMR  $\delta$  7.10 ppm (d, 1H,  $J = 9.3$ ),  $\delta$  7.32 ppm (s, 1H),  $\delta$  7.34 ppm (d, 1H,  $J = 9.6$ ),  $\delta$  9.60 ppm (s, 1H),  $\delta$  9.82 ppm (s, 1H). *p*-Hydroxybenzaldehyde:  $^1\text{H}$  NMR  $\delta$  6.94 ppm (d, 2H,  $J = 8.4$ ),  $\delta$  7.77 ppm (d, 1H,  $J = 8.7$ ),  $\delta$  9.79 ppm (s, 1H),  $\delta$  10.23 ppm (s, 1H).



**Figure S5** *o*-Benzoquinone: <sup>1</sup>H NMR δ 6.35 ppm (d, 2H, *J* = 12.0), δ 7.11 ppm (d, 2H, *J* = 12.0); 3-Hydroxymethyl-*o*-benzoquinone could also be observed with the proton resonance at δ 6.26 ppm (d, 2H, *J* = 10.0), however, the other peaks cannot be observed possibly overlapping with the resonance of IBA. After the isolation by chromatography on a silica gel column (CH<sub>3</sub>OH : CHCl<sub>3</sub> = 1 : 20 (v/v)), 3-hydroxymethyl-*o*-benzoquinone transferred to the reducing product 2,3-hydroxybenzyl alcohol, <sup>1</sup>H NMR (CD<sub>3</sub>OD, 300MHz, 25 °C): δ 4.78 ppm (s, 2H), δ 6.76 ppm (d, 1H, *J* = 7.8), δ 6.83 ppm (t, 1H, *J* = 7.8), δ 6.84 ppm (d, 1H, *J* = 8.1).



**Figure S6** 4-Hydroxymethyl-*o*-benzoquinone: <sup>1</sup>H NMR δ 4.35 ppm (s, 2H), δ 6.35 ppm (d, 1H, *J* = 10.0), δ 6.39 ppm (s, 1H), δ 7.00 ppm (d, 1H, *J* = 10.0). After the isolation by chromatography on a silica gel column (CH<sub>3</sub>OH : CHCl<sub>3</sub> = 1 : 20 (v/v)), 4-hydroxymethyl-*o*-benzoquinone transferred to the reducing product 3,4-hydroxybenzyl alcohol, <sup>1</sup>H NMR (CD<sub>3</sub>OD, 300MHz, 25 °C): δ 4.33 ppm (s, 2H), δ 6.55 ppm (d, 1H, *J* = 8.1), δ 6.60 ppm (d, 1H, *J* = 8.1), δ 6.64 ppm (s, 1H).



**Figure S6**  $^1\text{H}$  NMR Spectra of IBX oxidizing a) 2-hydroxybenzyl alcohol; b) 3-hydroxybenzyl alcohol; and c) 2-hydroxybenzyl alcohol in the absence of HemiQ[6] for 1.0 hour. The identification of aldehyde product was carried out by comparison with sample of authentic products, and the quinones were assigned by comparison with the spectra of original compounds.