**Supplementary Material**

**Large scale enzymatic reaction with P450<sub>BSβ</sub> and heptanoic acid.**

A large scale enzymatic reaction was carried out to obtain the product for NMR measurement. A solution of 4mM 1-methoxynaphthalene, 20mM heptanoic acid, 1µM P450<sub>BSβ</sub>, and 4mM H<sub>2</sub>O<sub>2</sub> in 0.1M K<sub>2</sub>HPO<sub>4</sub> buffer (pH 7.0) was incubated for 20 min at room temperature. The reaction mixture was added an equal amount of CH<sub>2</sub>Cl<sub>2</sub> and stirred for a few minutes. The two-phase mixture was filtrated to remove the denatured protein and the organic layer was separated. The product was purified by a silica gel column chromatography with ethylacetate/cyclohexane 1:9. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270MHz): δ = 8.41 (s, 2H, 3 and 3' -H), 8.17 (d, J=7.6, 2H, 5 and 5' -H), 7.80 (d, J=7.6, 2H, 8 and 8’ -H), 7.62 (t, J=7.6, 2H, 6 and 6’ -H), 7.48 (t, J=7.6, 2H, 7 and 7’ -H), 4.08 (s, 6H, -OCH3). UV-vis (λ<sub>abs</sub>, CHCl<sub>3</sub>): 281, 634.5 nm.

![Figure S1. The MALDI-TOF mass spectra of Russig’s blue obtained by the reaction with (A) H<sub>2</sub>¹⁶O<sub>2</sub> and (B) H<sub>2</sub>¹⁸O<sub>2</sub>.

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Figure S2. HPLC analysis of the extract of reaction mixture monitored at 280nm(a) and 614nm(b). HPLC chart of control experiments, purified russig’s blue, 1-methoxynaphthalene, 4-methoxy-1-naphthol, and 1-naphthol are also shown. Asterisk (*) indicates impurity in 1-methoxynaphthalene. The same reaction was conducted in the absence of P450$_{BS}$ or hydrogen peroxide as a control experiment. HPLC chart of control experiments are also shown. HPLC analysis was carried out on a Shimadzu LC-10AD equipped with a SPD-10A UV-visible detector and CHIRALCEL OD column (0.46cmφ x 25cm, DAICEL CHEMICAL INDUSTRIES, LTD.). The column was eluted with 85% of hexane and 15% 2-propanol at a flow rate of 0.3mL/min.