

## Electronic Supporting Information

### **Ferrocenated Nanocatalysts Derived from the Decomposition of Ferrocenium in Basic Solution and their Aerobic Activities for the Rapid Decolorization of Methylene Blue and the Facile Oxidation of Phenylboronic Acid**

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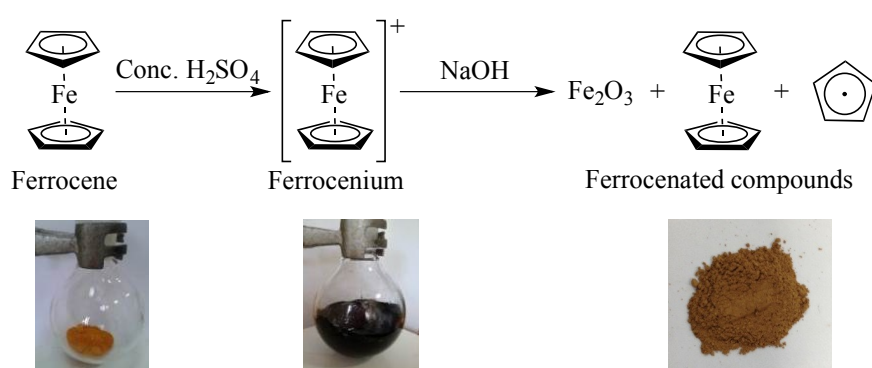
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### EPR spin trapping

Spin-trapped in phosphate buffer was prepared by dissolving Fc pH12 (3.04 mg) in 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO,  $7.64 \times 10^{-6}$  mol/dm<sup>3</sup>), phosphate buffer pH 7.4 (0.050 mol/dm<sup>3</sup>, 2 cm<sup>3</sup>), and incubating for 20 minutes. All EPR spectra were average of 1000 scans and simulated with WinSim 2002 program.

### Zeta potential analysis

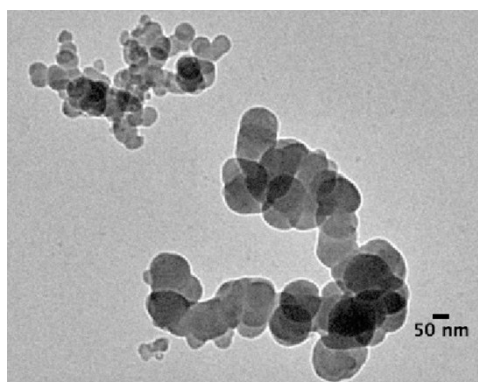
Ferrocenated compounds (10 mg) were dispersed in deionized water (5 cm<sup>3</sup>) and sonicated for 10 minutes. The mixture was filtrated syringe filter nylon 13 mm, 0.45 um with luer lock 100/pk.



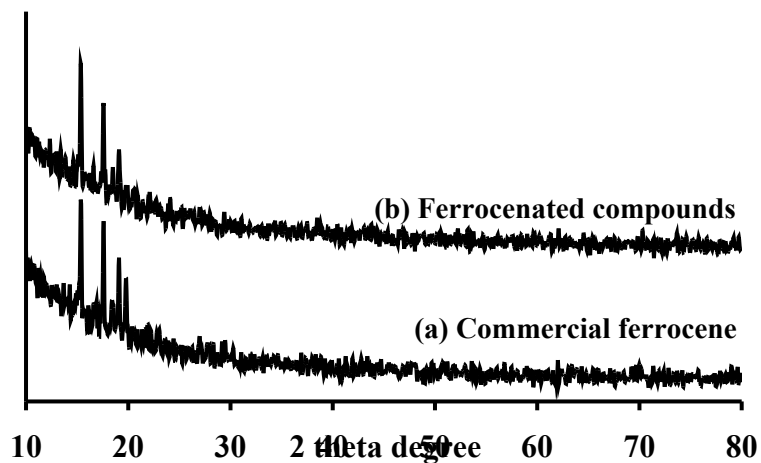
**Figure S1** The decomposition of ferrocenium species between electron exchange to ferrocene by sodium hydroxide in the presence of water to produce ferrocenated compounds.

### Transmission electron microscope

The sample for TEM measurement was prepared by dropping ferrocenated compounds suspended in an absolute ethanol onto a 300-mesh formvar coated copper grid. The solvent was evaporated at ambient pressure and temperature. The sample was obtained by a Tecnai G2 Sphera transmission electron microscope operated 80 kV.

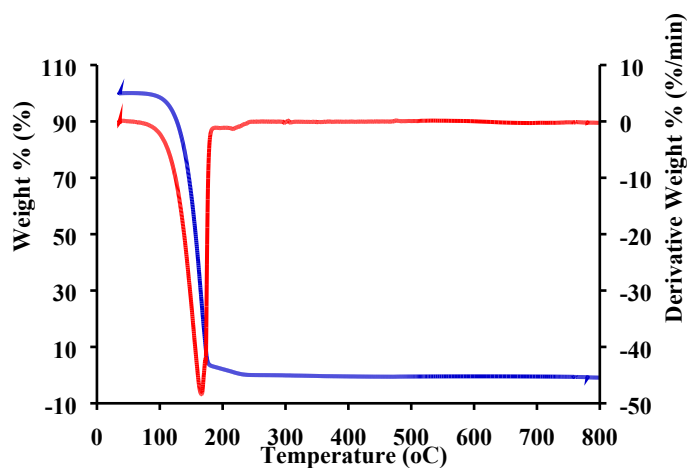


**Figure S2** TEM image of ferrocenated compounds.

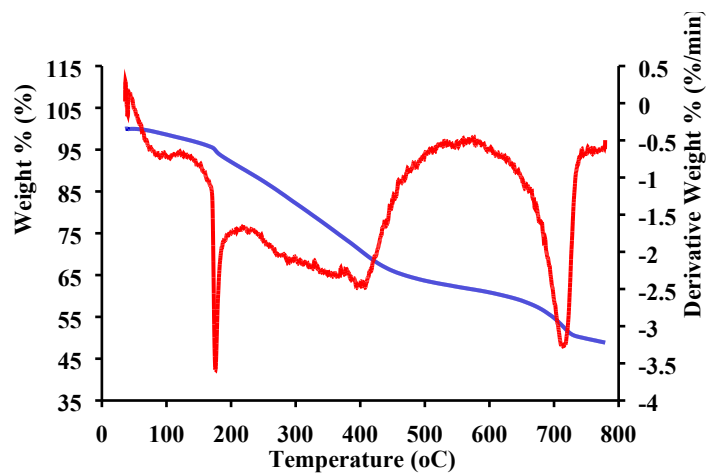


**Figure S3** XRD patterns of commercial ferrocene (a) and ferrocenated compounds (b).

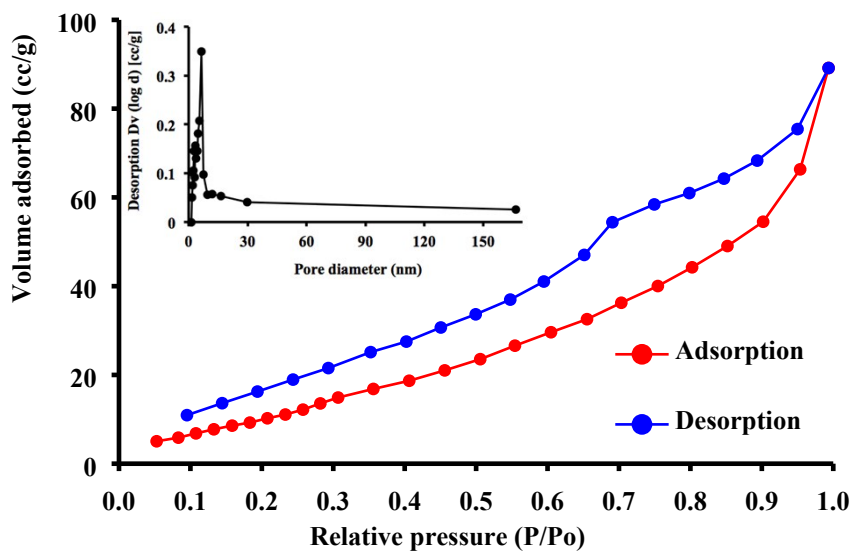
**(a) Commercial ferrocene**



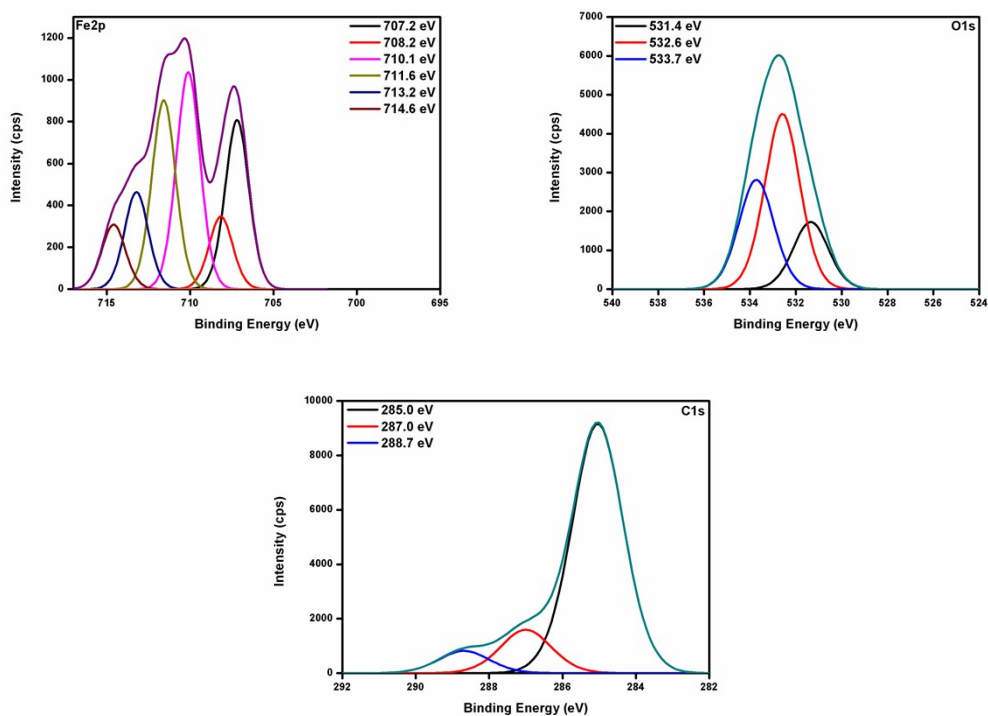
**(b) Ferrocenated compounds**



**Figure S4** DSC/TGA curve of commercial ferrocene (a) and ferrocenated compounds (b).



**Figure S5** Adsorption/desorption isotherms of nitrogen and pore size distribution of ferrocenated compounds.



**Figure S6** XPS spectra of Fe2p, O1s and C1s of ferrocenated compounds.

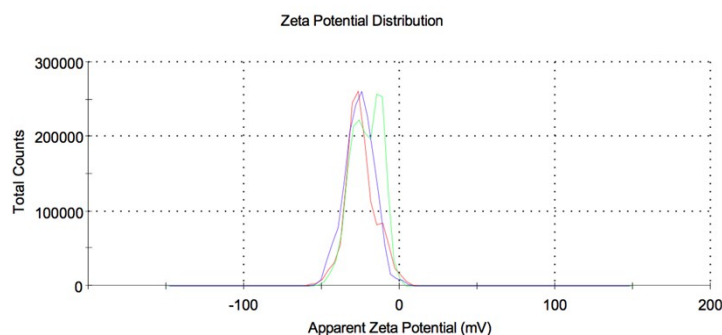
**Table S1** The binding energy of Fe2p, O1s and C1s of ferrocenated compounds

Sample	Fe2p binding energy (eV)					
	Fe2p <sub>3/2</sub> Ferrocene	Fe2p <sub>3/2</sub> (Fe <sub>3</sub> O <sub>4</sub> )	Fe <sup>3+</sup> 2p <sub>3/2</sub>	Fe <sup>3+</sup> 2p <sub>3/2</sub>	Fe <sup>3+</sup> 2p <sub>3/2</sub>	Fe <sup>3+</sup> 2p <sub>3/2</sub>
ferrocenated compounds	707.2	708.2	710.1	711.6	713.2	714.6

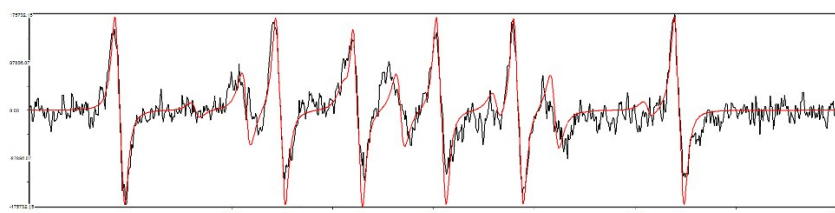
Sample	O1s binding energy (eV)		
	Fe–O	C–O	O–H
ferrocenated compounds	531.4	532.6	533.7

Sample	C1s binding energy (eV)		
	C–C in Cp <sup>a</sup>	C–O	O–C–C
ferrocenated compounds	285.0	287.0	288.7

<sup>a</sup>Cp = C<sub>5</sub>H<sub>5</sub>



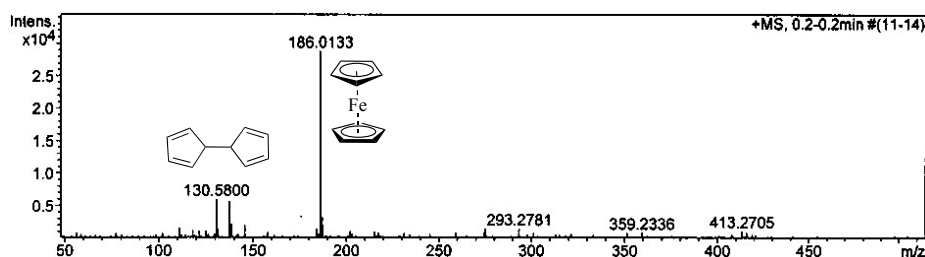
**Figure S7** Zeta potential distribution of ferrocenated compounds in DI water.



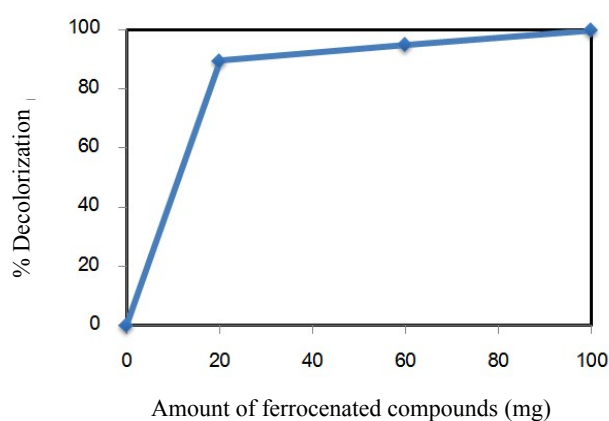
**Figure S8** The simulated EPR spectrum of ferrocenated compounds described the existence of hydroxyl and superoxide radical intermediates.

**Table S2** EPR hyperfine splitting for radical intermediates in the reaction of ferrocenated compounds with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and phosphate buffer pH 7.4. The spectrum was derived from WinSim 2002 program

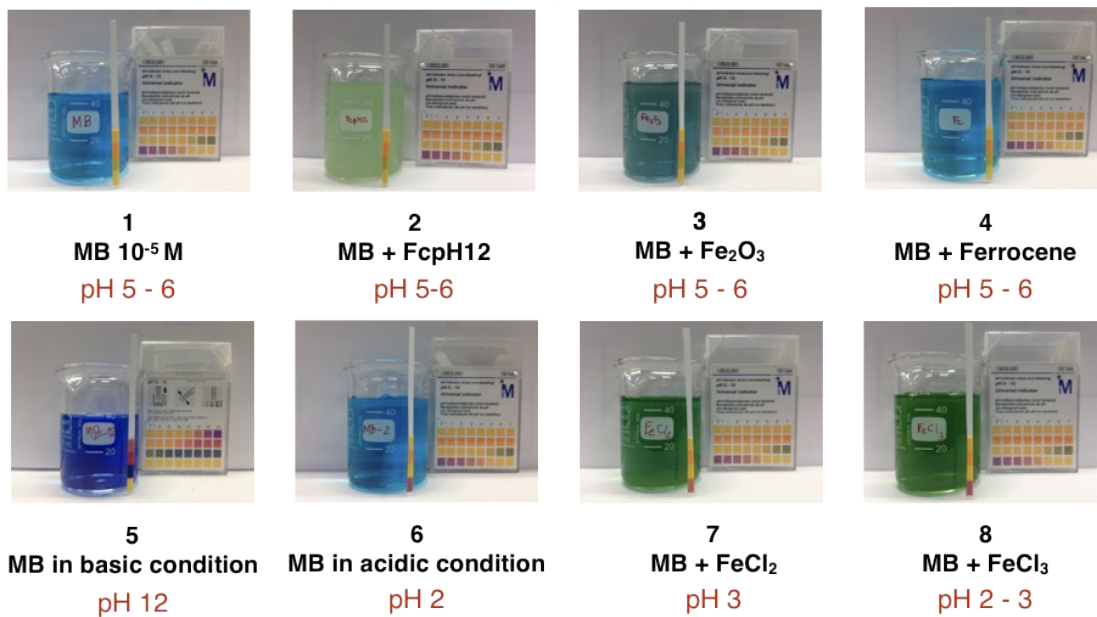
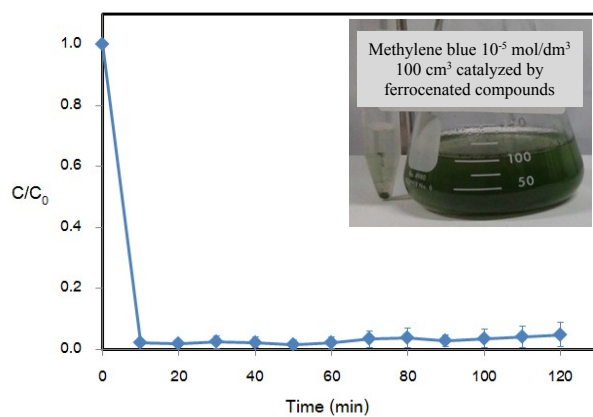
Sample	DMPO adducts	Hyperfine splitting of nitrogen (G)	Hyperfine splitting of hydrogen (G)
ferrocenated compounds	DMPO-OOH (71%)	15.16 ( $a_N$ )	22.16 ( $a_{H1}$ ), 0.47 ( $a_{H2}$ )
	DMPOX (21%)	14.37 ( $a_N$ )	-
	DMPO-OH (8%)	14.50 ( $a_N$ )	14.47 ( $a_H$ )
Reused ferrocenated compounds from the 12 <sup>th</sup> -cycle	DMPO-OOH (47%)	15.27 ( $a_N$ )	22.26 ( $a_{H1}$ ), 0.51 ( $a_{H2}$ )
	DMPOX (43%)	14.32 ( $a_N$ )	-
	DMPO-OH (10%)	14.49 ( $a_N$ )	14.55 ( $a_H$ )



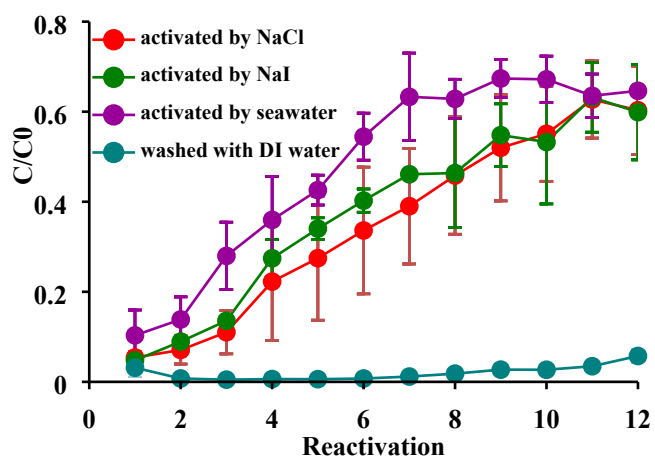
**Figure S9** Electrospray ionization mass spectrometry (ESI-MS) spectrum of ferrocenated compounds in water.



**Figure S10** The effect of amount of ferrocenated compounds on decolorization of methylene blue without addition of hydrogen peroxide and irradiation of light (2 hours).

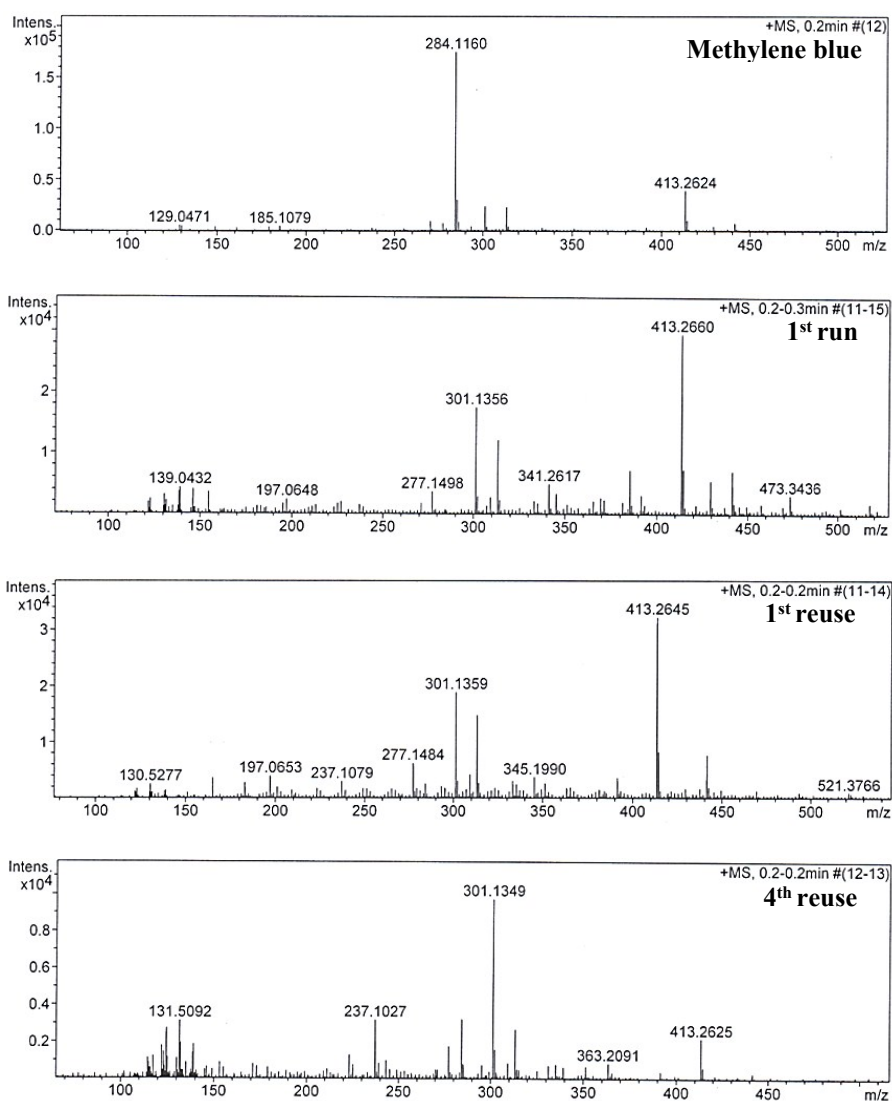


**Figure S11** Catalytic activity of ferrocenated compounds decolorized methylene blue without addition of hydrogen peroxide and irradiation of light. The error bar plot by collected the reaction for 3 times. And the pH test of methylene blue with the prepared catalyst, iron oxide, ferrocene, and iron salts.

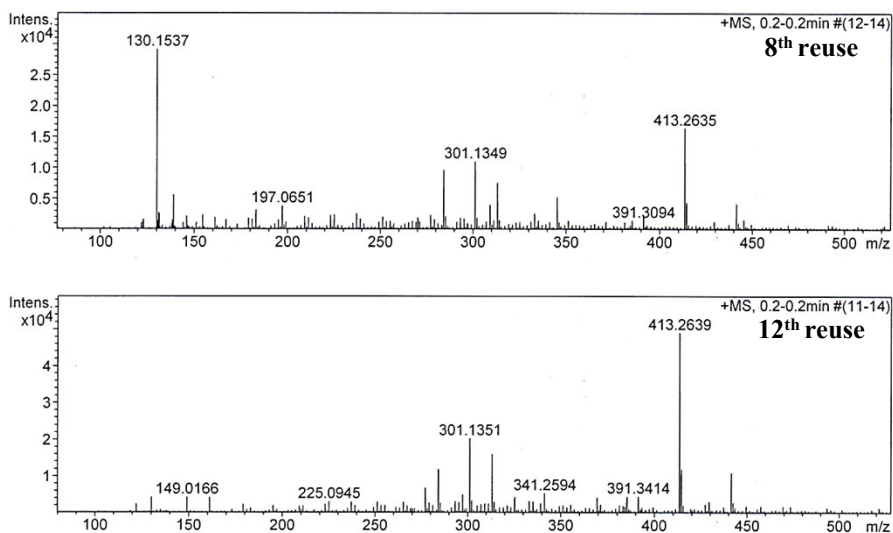


**Figure S12** Concentration of methylene blue after reactivation ( $C/C_0$ ) with DI water, 0.1 mol/dm<sup>3</sup> NaCl, 0.1 mol/dm<sup>3</sup> NaI and seawater.

The decolorization of methylene blue on ferrocenated compounds revealed in the ESI-MS analysis. The signal of methylene blue before the decolorization was observed with  $m/z$  of 284. At the finished reaction, the appearance of decomposition in methylene blue was observed with  $m/z$  of 301. Moreover, the active species remained in the stable form of dihydrofulvalene with  $m/z$  of 130 as shown in Figure S10.







**Figure S13** ESI-MS spectra of decolorization of methylene blue catalyzed by ferrocenated compounds with  $0.1 \text{ mol/dm}^3$  NaCl as reactivator.

Table S3. Oxidation of phenylboronic acid with extra hydrogen peroxide and no light.

Entry	Catalyst	H <sub>2</sub> O <sub>2</sub> (equiv.)	Yield <sup>b</sup> (%)
1	-	-	0
2	-	1	29
3	Ferrocene (100 mg)	-	1
4	Ferrocene (100 mg)	1	28
5	Fe <sub>2</sub> O <sub>3</sub> (100 mg)	-	4
6	Fe <sub>2</sub> O <sub>3</sub> (100 mg)	1	29

<sup>a</sup> Reaction conditions: phenylboronic acid (0.25 mmol), K<sub>2</sub>CO<sub>3</sub> (0.75 mmol), H<sub>2</sub>O (10 cm<sup>3</sup>) under atmospheric condition at 80 °C for 24 h without lights.

<sup>b</sup> %Yield of phenol by GC-MS analysis with hexadecane as internal standard