Supporting Information

Synthesis of SiO_2 Coated Zero-valent Iron/Palladium Bimetallic Nanoparticles and Application in a Nano-biological Combined System for 2,2'4,4'-Tetrabromodiphenyl ether Degradation

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Preparation of resting cells

P. putida was incubated in 150 mL MSM in 500 mL Erlenmeyer flask with 1 g L^{-1} and 0.5 g L^{-1} of glucose at 30 ºC for 72 h under a rotary shaker at 150 rpm. For the preparation of resting cells of *P. putida*, the whole culture suspension was harvested and separated by centrifugation at 6 000 rpm for 10 min. The separated cells were washed three times with sterile phosphate buffer (pH 7.00) and suspended in MSM.

Synthesis of SiO_2-coated zero-valent iron/palladium bimetallic nanoparticles

4 g of $FeSO_4 \cdot 7H_2O$ was added into a three-neck round flask containing 300 mL H_2O/ethyl alcohol solution (V/V=80:20). Black iron nanoparticles formed when $NaBH_4$ solution (0.4g dissolved in 50 mL H_2O) was added dropwise under nitrogen atmosphere at 1 000 rpm. After stirring for 30 min, 2.0 mL of chloropalladic acid solution (1.18 g Pd L^{-1}) was added to the black suspension liquid, in which, the dose of palladium for coating the nZVI particles was 0.3% by iron weight. After 20 min, 2 mL tetraethyl orthosilicate (TEOS) was added to the flask and the flask was stirred for 20 min. Finally, the SiO_2-nZVI/Pd particles were suspended in the deoxygenated water to form nZVI/Pd slurry (10 g L^{-1}) for use after washed thrice with ethyl alcohol and deoxygenated water.

Extraction of samples

Before the extraction, the bottles were added 2 mL 1M H_2SO_4. When the nZVI particles were dissolved, the whole bottle was extracted with 20 mL of dichloromethane thrice via Vortex (IKA, Germany) for 5 min. After removing water with sodium sulfate, the final volume of the extract was adjusted to 20 mL with solvent vaporization through Nitrogen Evaporators (Organomation, USA). Before analyzed, all the samples were treated with 0.22 μm nylon filters.

Analytical methods

Analysis of BDE47 and debromination products

The concentrations of BDE47 and DE were determined by ultra performance liquid chromatography (UPLC, Waters ACQUITY UPLC system, America) equipped with a photo-diode array (PDA) detector and a ACQUITY UPLC BEH Amide Column (150mm×2.1mm) at 226 nm. The mobile phase was methanol/ultrapure water solution (70:30, v/v) delivered at 0.3 mL/min and 30 ºC. The injection volume was 2 μL. The quantification was performed with the calibration curves of BDE47 and DE standards with 0.993 and 0.996 of correlation coefficient in range of 0.2 to 20 mg L^{-1}.

The concentrations of debromination products were determined by Thermo Trace GC Ultra instrument coupled to a Thermo DSQ II mass spectrometer (GC-MS, Thermo Electron Corporation, Waltham, USA). A 30 DB-5ms GC column (0.25 mm i.d. × 0.25 μm film thickness) and a constant flow of Helium at 1.0 mL/min were used to separate the by-products. The MS was run in electron ionization (EI) mode and sim scan with solvent delay of 5 min. The whole sim scan program was as follows: scanning the characteristic ions (m/z) of 170, 141, 77 and 51 during 5-11 min, then 250, 248, 169, 141 and 77 in 11-14 min, 328, 219, 168, 140, 139 and 75 from 14 to 17 min, 408, 407, 406, 248, 246, 139 and 75 during 17-20 min, finally 486, 326, 217, 138 and 75 in 20-22 min. While the temperature program of the oven was firstly set to 80 ºC (held for 2 min), then rose to 260 ºC with 12 ºC/min, and finally increased to 310 ºC with 50 ºC/min and held for 4 min. Splitless injection of 1 μL sample was performed automatically at 280 ºC and the transfer line temperature were set 250 ºC. Prior to GC-MS analysis, the whole flask contained PBDEs were extracted with 30 mL dichloromethane thrice with Vortex (IKA, Germany) for 5 min. After removing water with anhydrous sodium sulfate, the extracts were combined and concentrated to 5 mL with solvent vaporization through Nitrogen Evaporators (Organomation, USA). Before analyzed, all the samples were treated with 0.22 μm glass fiber filters.

Analysis products of biodegradation of DE

The intermediates during biodegradation of DE were analyzed by GC-MS in full scan model (50-900 m/z of ions ranges) and the pre-treatment process was similar to that of PBDEs. The temperature program of the oven was firstly set to 60 ºC, then rose to 250 ºC with 10 ºC/min, and held for 5 min. Splitless injection of 1 μL sample was performed automatically at 250 ºC and the transfer line temperature were set 200 ºC. The solvent delay was set as 5 min.

Analysis of Br ions

The samples were centrifuged at 6000 rpm for 10 min and then treated with 0.22 μm polyether sulfone filters. The concentration of bromide ion (Br^-) was determined by an ion-chromatography system (ICS-90, Dionex). 20 μL of sample was injected into a Dionex AS4A-SC 4X 250 mm column (150 mm length × 4.6 mm i.d.) with a Dionex guard column. The column temperature was set at 40 °C. A solution containing 9 mM Na_2CO_3 as the mobile phase was delivered at a flow rate of 1.0 mL min^{-1}. The suppressor current was set at 60 mA.

Standard protocol of sample preparation for TEM analysis

The samples containing *P. putida* cells and nanoparticles were prepared. A drop of the samples was placed on a glow-discharged Formvar-coated copper grid for 2 min. After the excess liquid was drained off by filter paper, the grids were exposed to aqueous 1% phosphotungstic acid for another 2 min. The residual staining solution was then removed, and the samples were immediately transferred to TEM for inspection.

Standard protocol of biological slices preparation for TEM analysis

The TEM specimens of *P. putida* cells were prepared by the following procedures. The native and treated cells were quickly fixed in the mixture solution (4% of paraformaldehyde and 2.5% of glutaraldehyde) for 12 h at 4 °C. Followed by washing

three times, the samples were postfixed with 1% osmium tetroxide in 0.05M sodium cacodylate buffer for 2 h. After fixation, the samples were concentrated by centrifugation at 6000 rpm for 2 min and washed twice with PBS buffer. The concentrated cells were dehydrated with sequential treatment with 30, 50, 70, 80, 90, and 100% ethanol for 10 min. The cells were then infiltrated and embedded in Spurr's resin with propylene oxide (treatment with 3:1, 2:1, 1:1, 1:2, and 1:3 of propylene oxide/Spurr's resin mixtures for 30min each, and100% Spurr's resin for 25 h). The samples, filled with Spurr's resin, were cured overnight at 70 °C to form sample blocks. The polymerized blocks were sectioned using an ultramicrotome (MT-X, RMC), and the thin sections were stained in 2% uranyl acetate and Reynold's lead citrate and examined by TEM at 80 kV accelerating potential.

Fig.S1

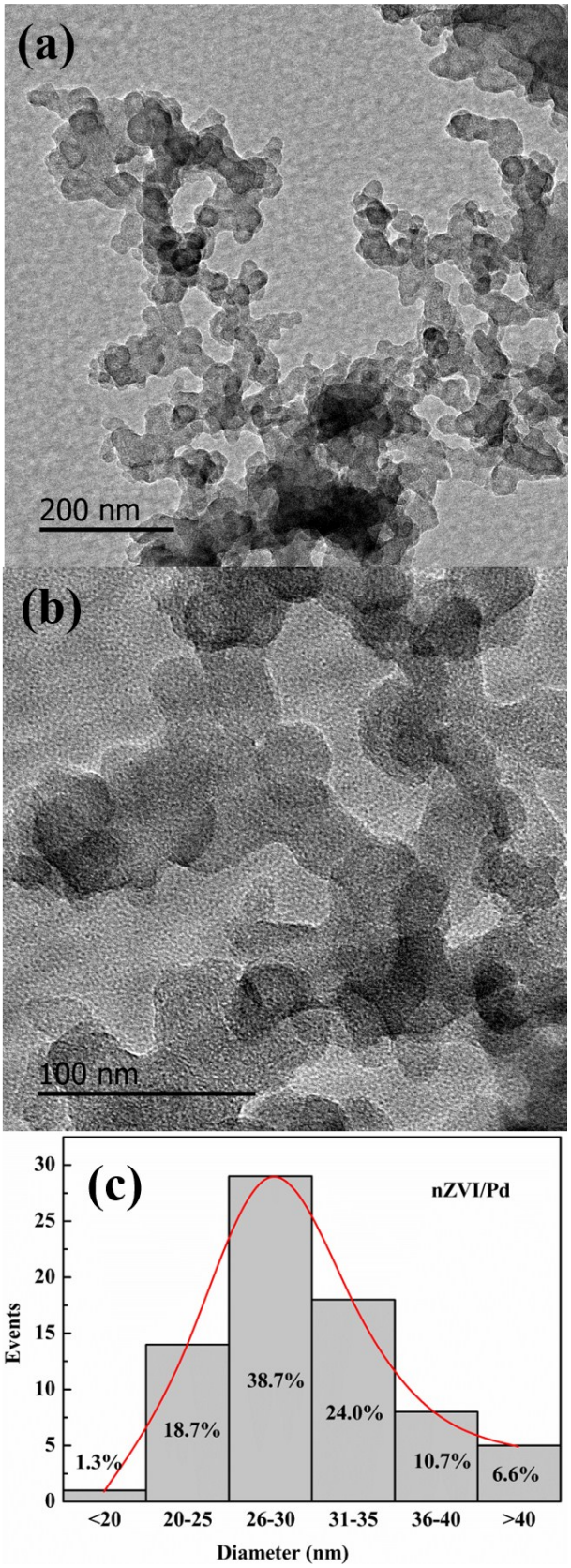

Fig.S1 TEM images (a and b) and size distribution (c) of fresh nZVI/Pd particles.

Fig.S2

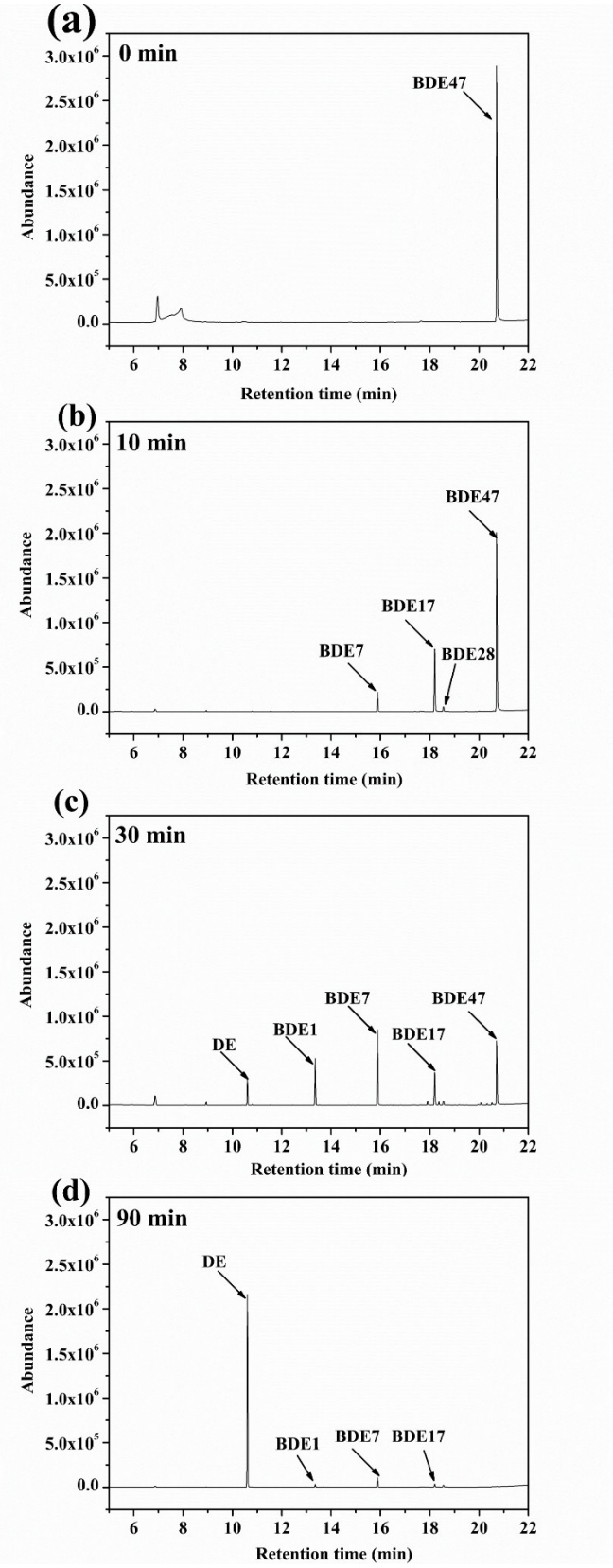

Fig.S2 GC-MS chromatographs of BDE47 and the by-products during anaerobic debromination by SiO_2-nZVI/Pd at different time

Fig.S3

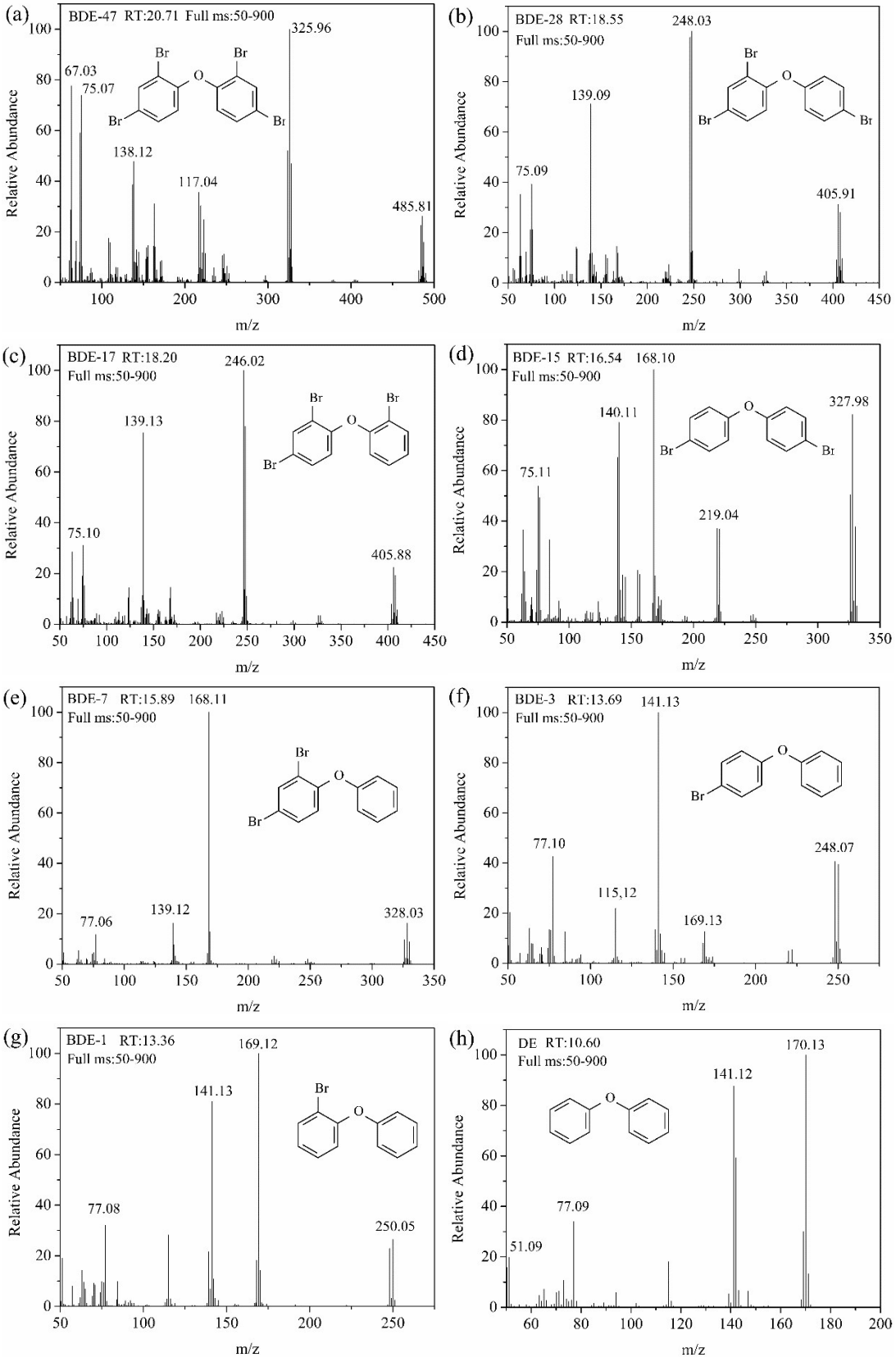

Fig.S3 Mass spectra of by-products of BDE47 degradation during anaerobic debromination

Fig.S4

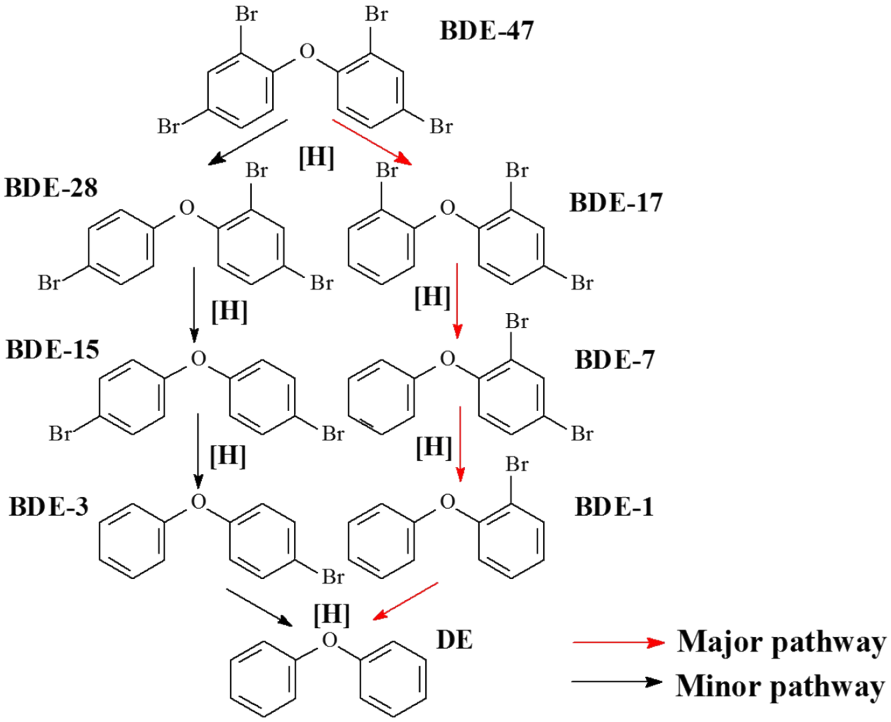

Fig.S4 Anaerobic debromination mechanism of BDE47 by SiO_2-nZVI/Pd particles.

Fig.S5

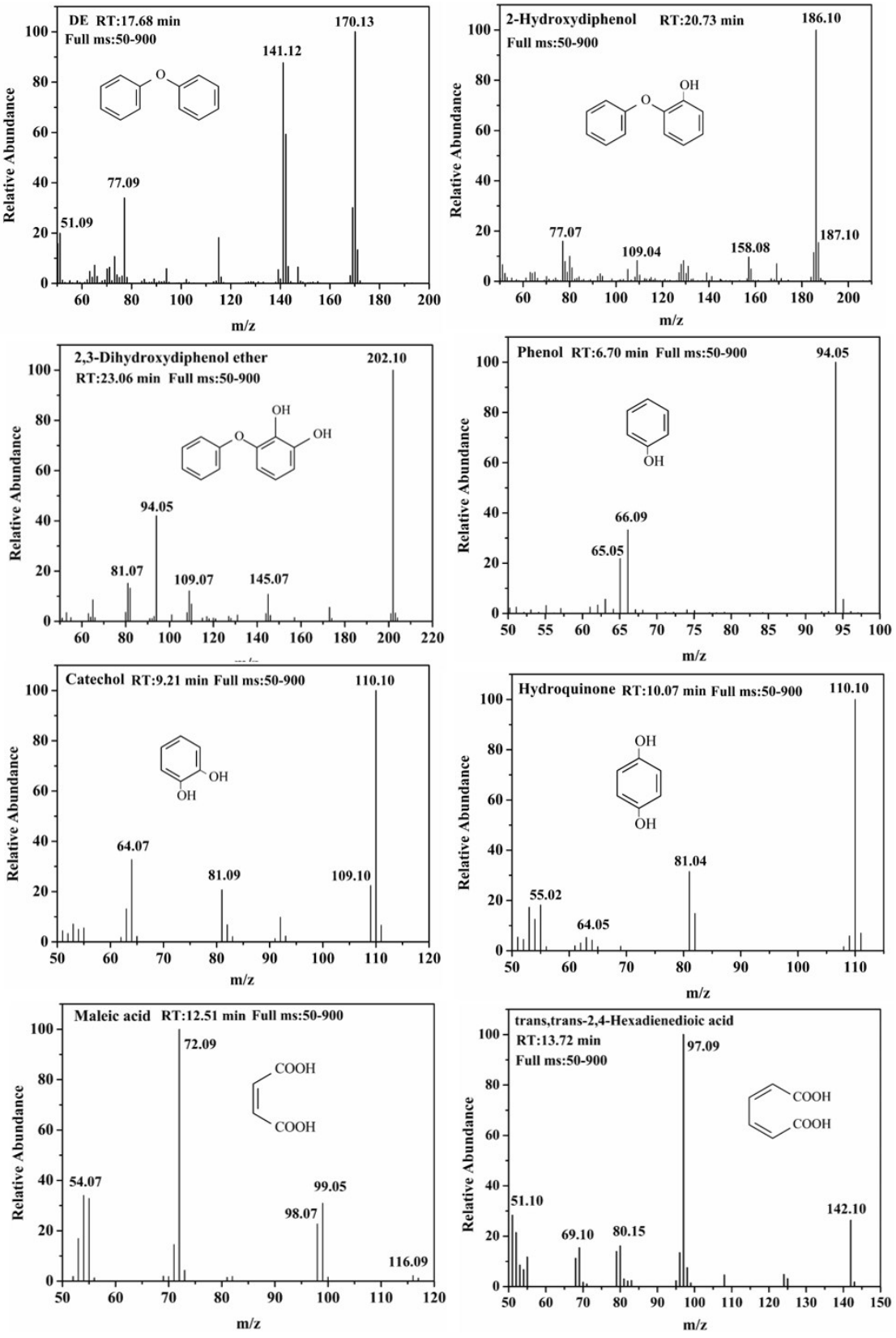

Fig.S5 Mass spectra of by-products of DE degradation by *P. putida* strain