

Supporting information for

Manganese oxides-mediated halogenation of carbazole under marine-related conditions

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Table S1. The detail information of carbazole and PHCZ congeners

Full name	Abbreviation	Vendor	Purity	CAS
Carbazole	/	Sigma-Aldrich (St. Louis, Missouri, USA)	≥95%	86-74-8
3-Bromo-9H-carbazole	3-BCZ	Sigma-Aldrich (St. Louis, Missouri, USA)	97%	1592-95-6
3-Chloro-9H-carbazole	3-CCZ	Toronto Research Chemicals (Toronto, Ontario, Canada)	>98%	2732-25-4
3,6-Dibromo-9H-carbazole	36-BCZ	Sigma-Aldrich (St. Louis, Missouri, USA)	97%	6825-20-3
3,6-Dichloro-9H-carbazole	36-CCZ	Sigma-Aldrich (St. Louis, Missouri, USA)	/	5599-71-3
1,3,6-Tribromo-9H-carbazole	136-BCZ	Wellington Laboratories (Guelph, Ontario, Canada)	>98%	55119-10-3
1-Bromo-3,6-dichloro-9H-carbazole	1-B-36CCZ	Wellington Laboratories (Guelph, Ontario, Canada)	>98%	100125-05-1
1,3,6,8-Tetrabromo-9H-carbazole	1368-BCZ	Toronto Research Chemicals (Toronto, Ontario, Canada)	95%	55119-09-0
1,3,6,8-Tetrachloro-9H-carbazole	1368-CCZ	Wellington Laboratories (Guelph, Ontario, Canada)	>98%	58910-96-6
1,8-Dibromo-3,6-dichloro-9H-carbazole	18-B-36-CCZ	Wellington Laboratories (Guelph, Ontario, Canada)	>98%	100131-03-1
2,3,6,7-Tetrachloro-9H-carbazole	2367-CCZ	Wellington Laboratories (Guelph, Ontario, Canada)	>98%	697298-02-5

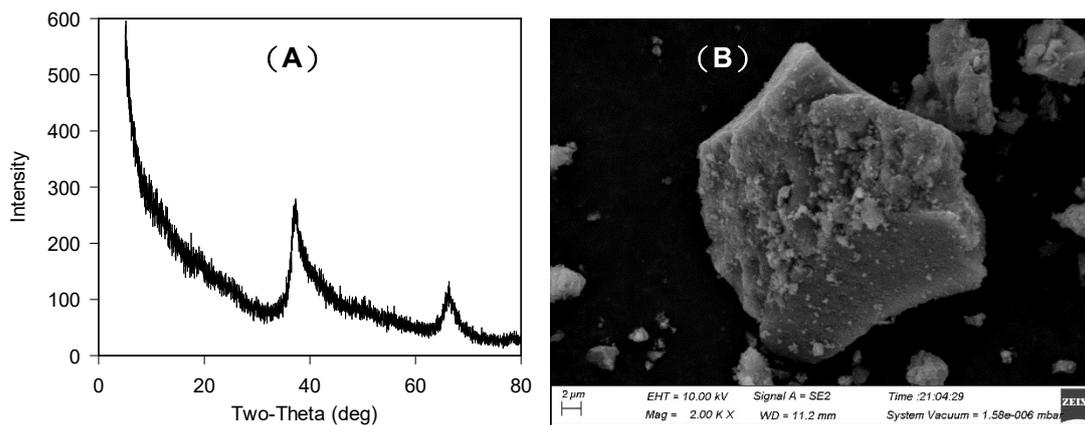


Figure S1. Scanning electron microscopy (A) and X-ray diffraction (B) analyses of the synthesized δ -MnO₂.

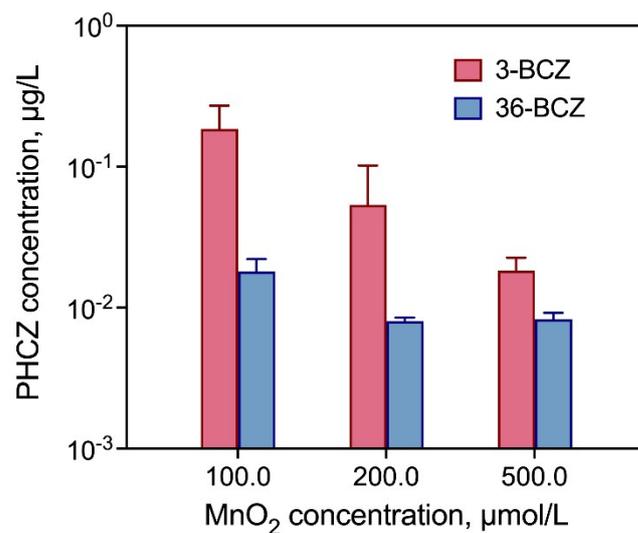


Figure S2. Effect of the concentration of δ -MnO₂ on PHCZs production. The reaction was carried out in 0.8 mmol/L NaBr solution with pH value of 8.2 at 25°C. The initial concentration of carbazole was 5 µmol/L. The reaction time was 24 h.

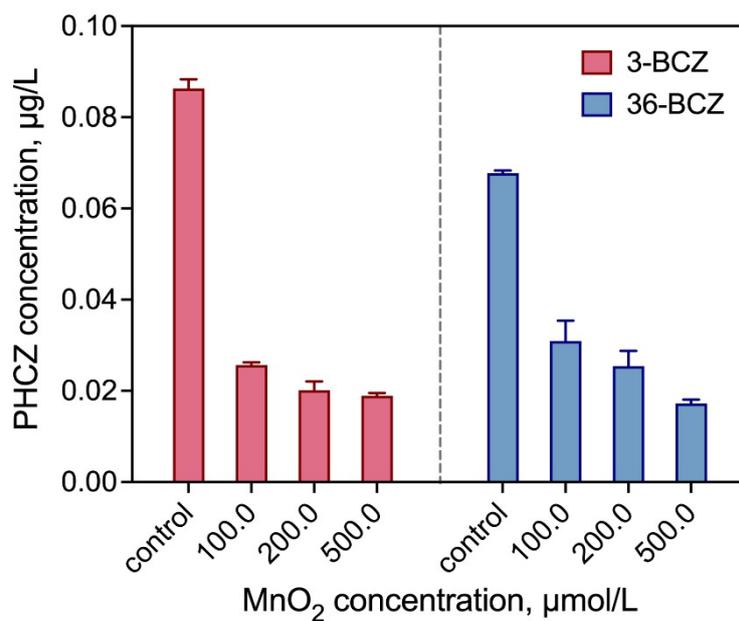


Figure S3. The degradation of 3-BCZ and 36-BCZ by δ -MnO₂. The reaction was carried out in 0.8 mmol/L NaBr solution with pH value of 8.2 at 25°C. The initial concentrations of 3-BCZ and 36-BCZ were 0.1 μmol/L. The reaction time was 24 h. The control experiment was conducted in the absence of δ -MnO₂.

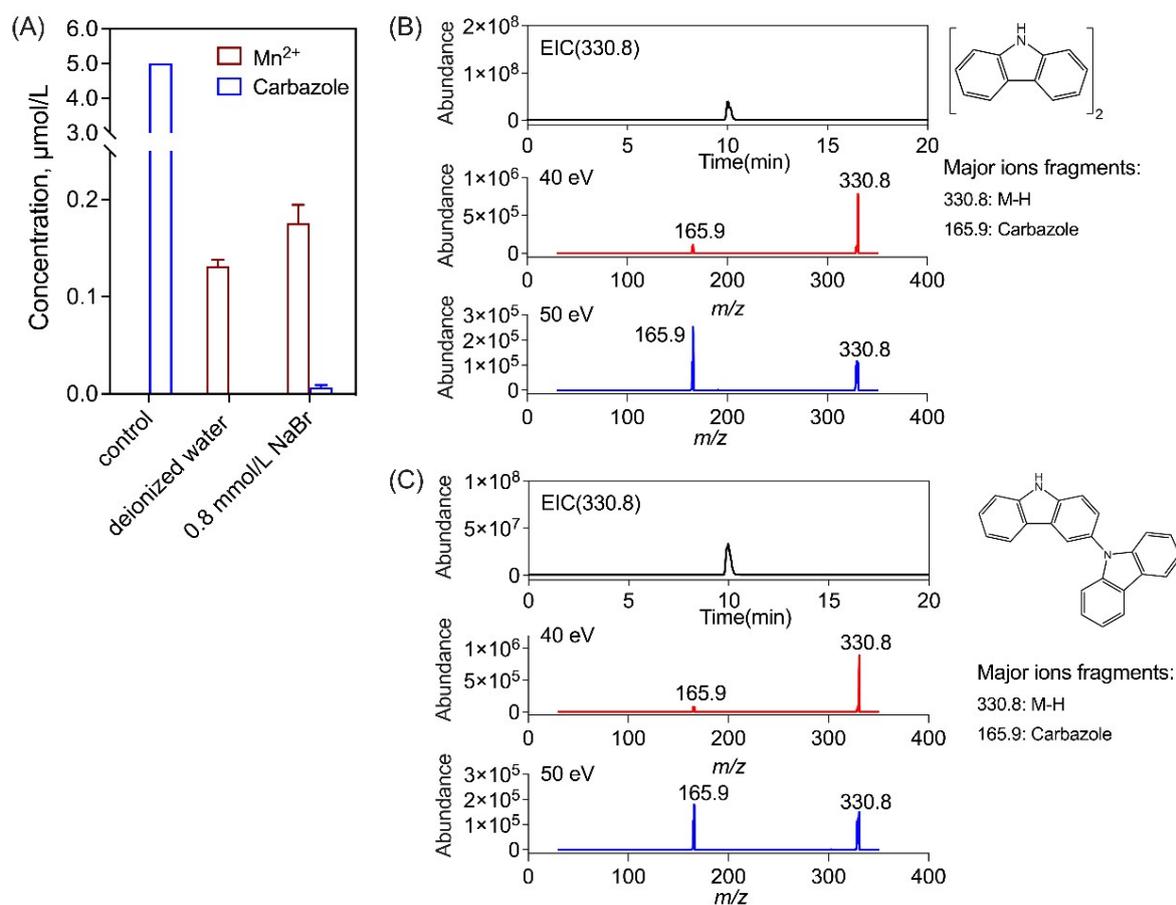


Figure S4. $\delta\text{-MnO}_2$ -mediated the oxidative transformation of carbazole (A) transformation of the substrate carbazole; (B) identification of unknown carbazole dimer using LC-MS/MS; (C) identification of 3,9'-bicarbazole using LC-MS/MS.

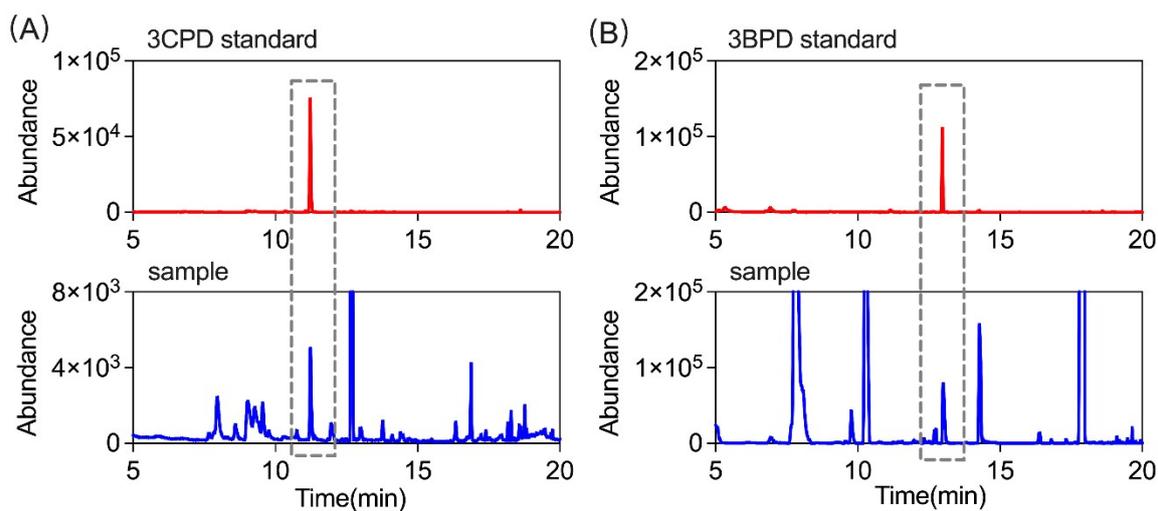


Figure S5. RHS detection with GC-MS using allyl alcohol as chemical probe (A) detection of RCS; (B) detection of RBS. Panel (A): the reaction system was 0.54 mol/L NaCl. Panel (B) the reaction system was 0.8 mmol/L NaBr. The reaction time was 24 h. The reaction temperature was 25°C.