

Supporting Information

**An Exceptionally-Facile Two-Step Structural Isomerization and Detoxication via a Water-Assisted Double Lossen Rearrangement**

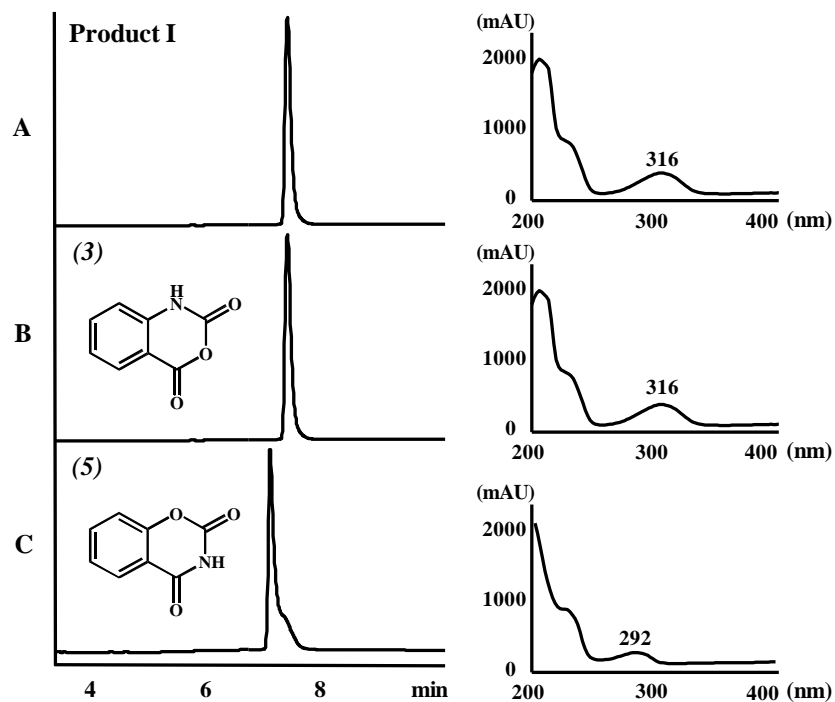
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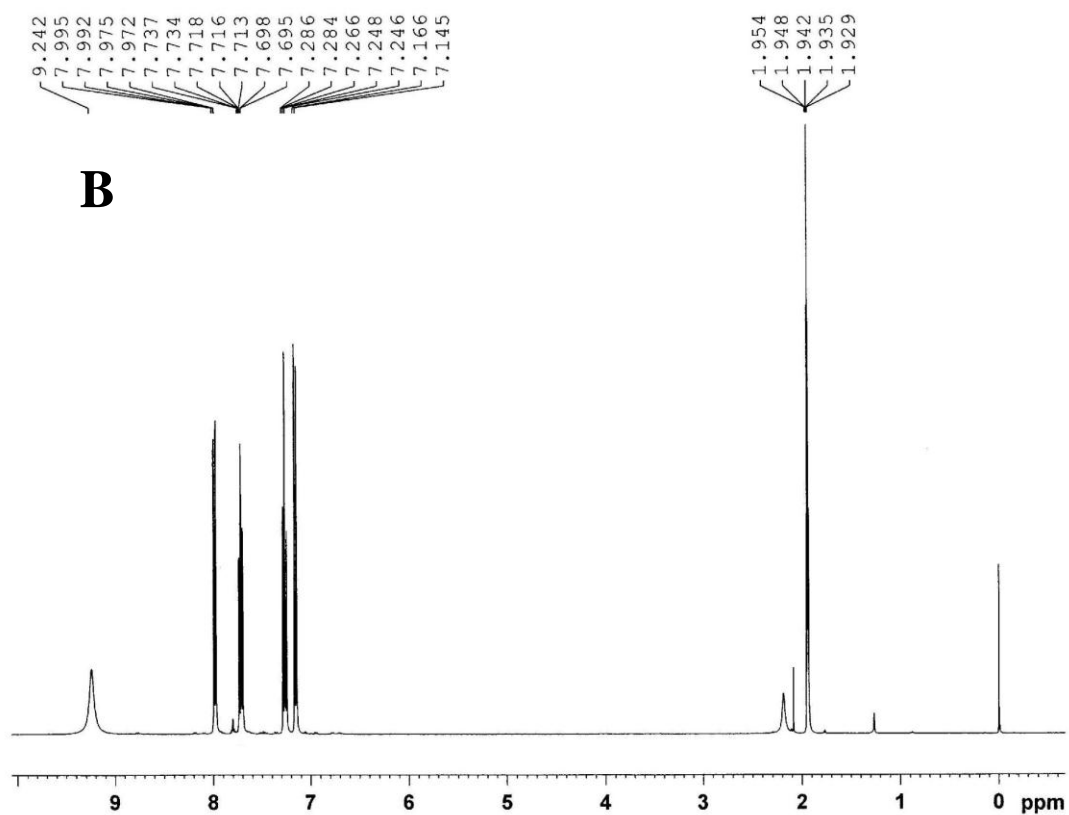
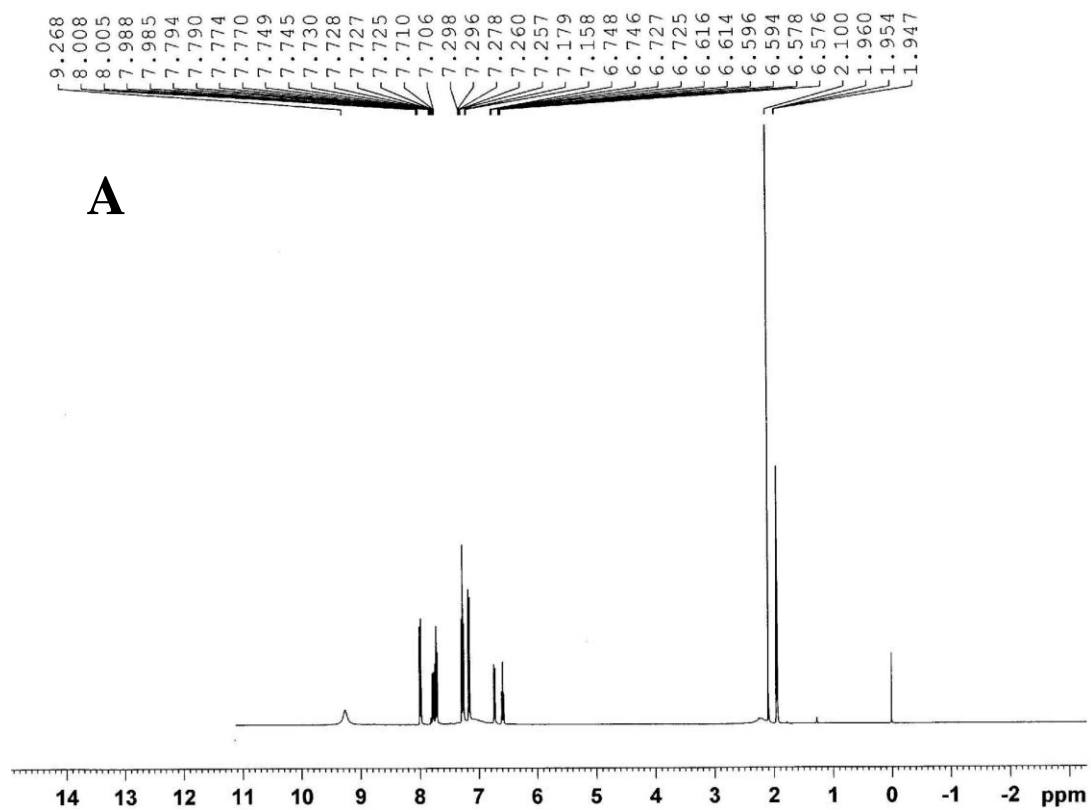
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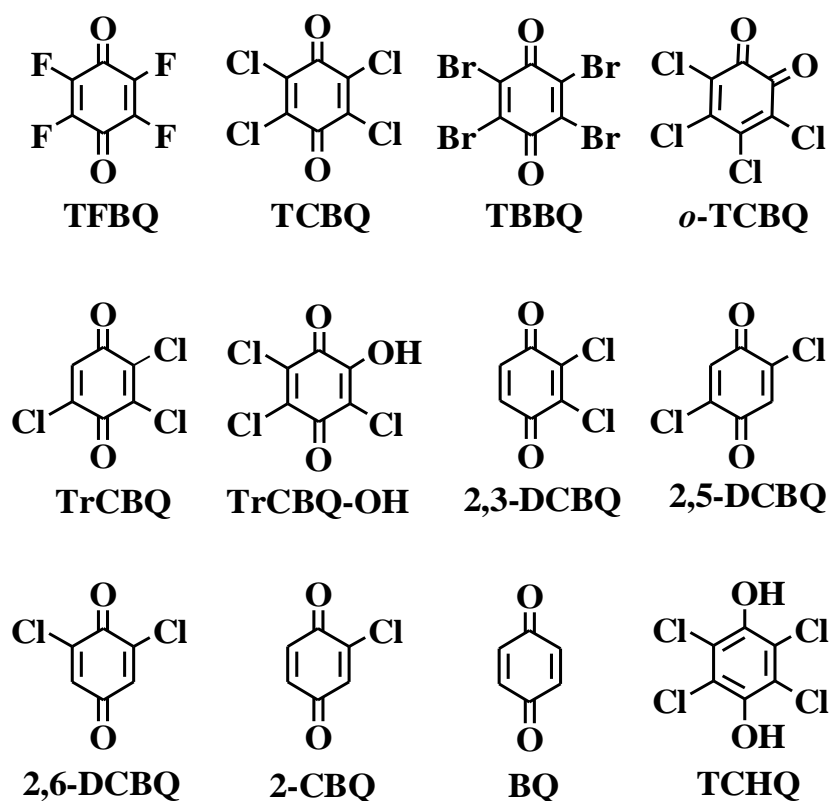
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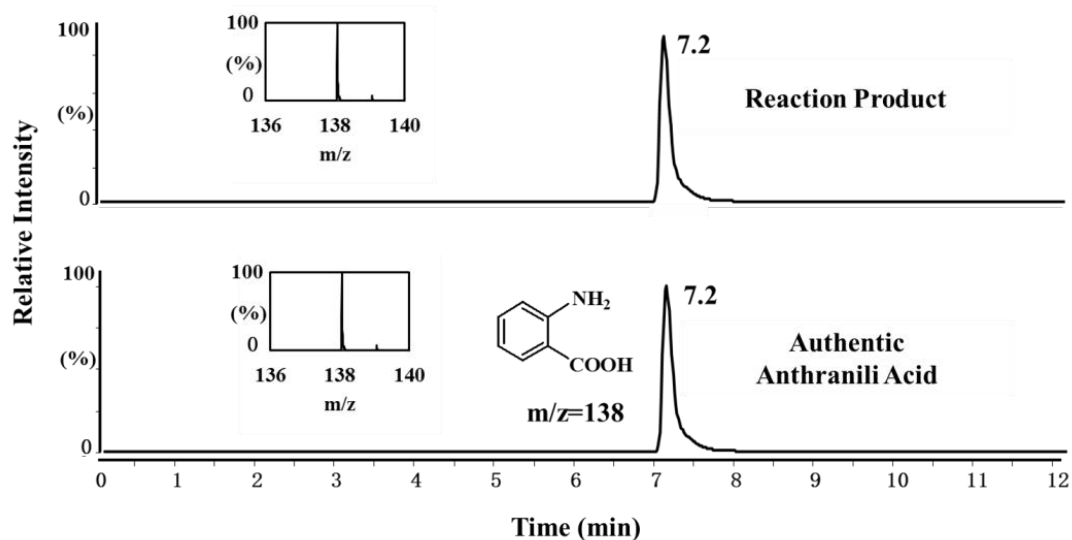
**Figure S1. Product I and (3) have the same retention time and UV spectrum, while the retention time and UV spectrum between Product I and (5) are different. These HPLC data show that Product I is (3). (A) Product I. (B) (3) (Isatoic anhydride). (C) (5).**



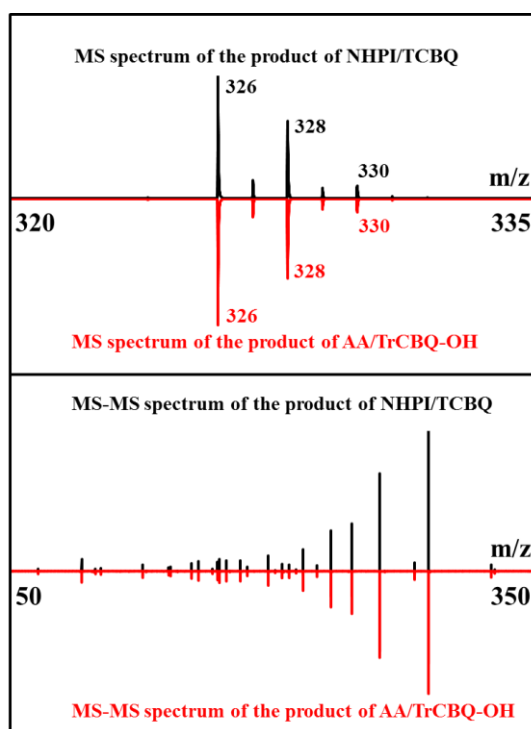
**Figure S2. NMR spectra of (A) isolated Product I; (B) authentic isatoic anhydride.**



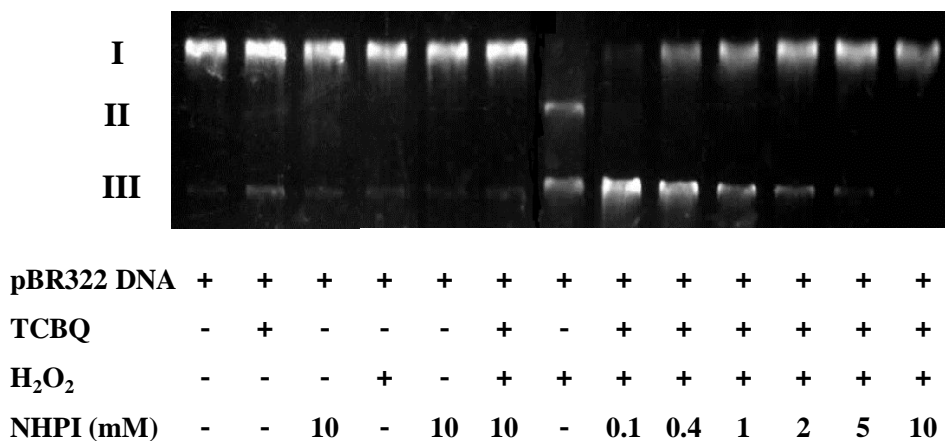
**Figure S3.** Chemical structures of halogenated quinoid compounds used in this study.



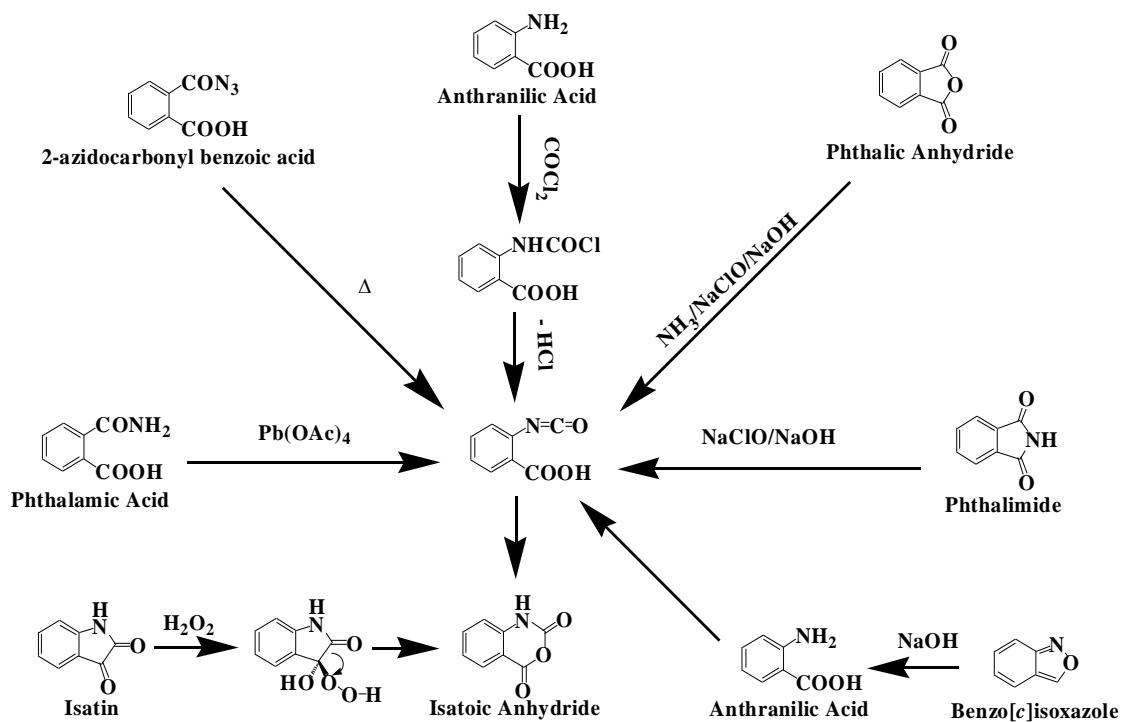
**Figure S4.** The hydrolysis product of IA is confirmed to be anthranilic acid (AA) by comparison with the authentic standard. The hydrolysis product of IA shows the same retention time and *m/z* in the HPLC-MS data.



**Figure S5. The MS and MSMS spectra of Product II.** The MS and MSMS data of Product II of NHPI/TCBQ match well with those of the reaction of AA/TrCBQ-OH, which means that Product II is as the same as the nucleophilic product of AA/TrCBQ-OH.



**Figure S6. Protection by NHPI against TCBQ/H<sub>2</sub>O<sub>2</sub>-induced DNA damage.** The concentrations: pBR322 DNA, 5 $\mu$ g/mL; TCBQ, 0.1 mM; H<sub>2</sub>O<sub>2</sub>, 10 mM.



**Scheme S1.** The most commonly-used methods for the synthesis of isatoic anhydride.

**Table S1.** The FT-ICR-MS data of the products of the reaction of NHPI and TCBQ.

Meas. m/z	#	Formula	Score	m/z	Err [mDa]	Err [ppm]	mSigma	rdb	E?conf	N-rule
162.01966	1	C <sub>8</sub> H <sub>4</sub> NO <sub>3</sub>	100.0	162.01967	0.00	0.02	9.1	7.5	Even	Ok
325.96277	2	C <sub>13</sub> H <sub>6</sub> Cl <sub>2</sub> NO <sub>5</sub>	100.0	325.96285	0.08	0.26	28.3	10.5	Even	Ok
351.94198	3	C <sub>14</sub> H <sub>4</sub> Cl <sub>2</sub> NO <sub>6</sub>	100.0	351.94212	0.14	0.39	90.1	12.5	Even	Ok