Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting Information

Phototransformation of benzimidazole and thiabendazole inside cucurbit[8]uril

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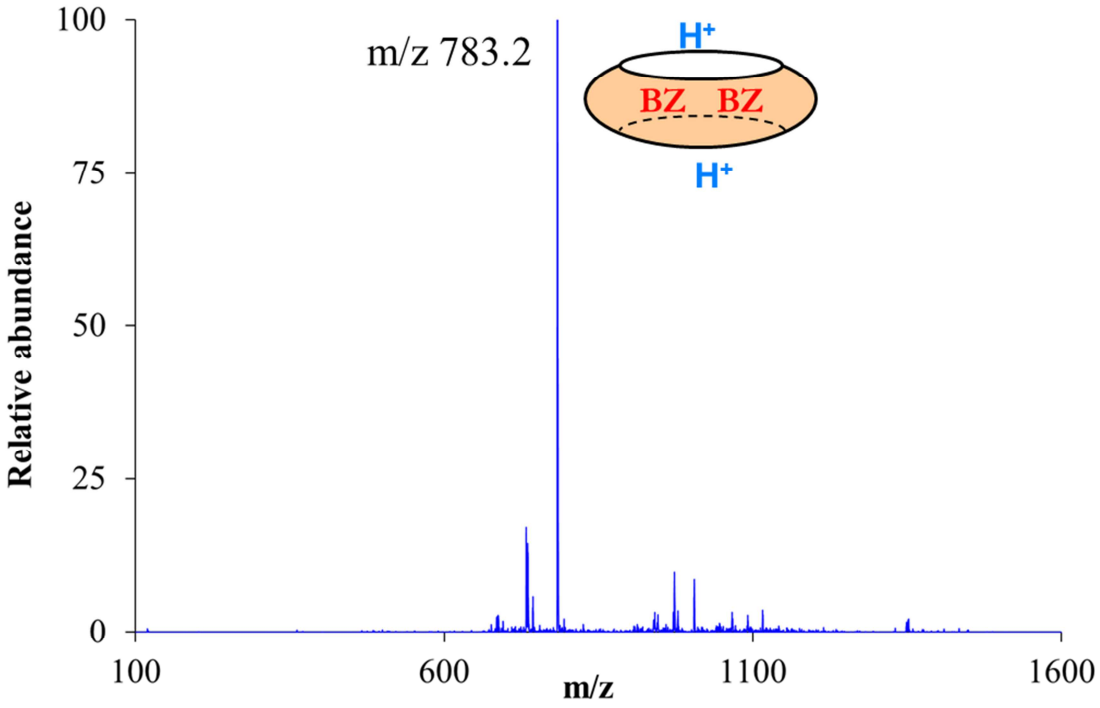

Figure S1. ESI-MS spectum (full scan) of an aqueous solutions of BZ and CB8 (1:1, stoichiometry) at pH ~ 6.5, 25 μM) Assignment: 783.2 $[CB8+2BZ+2H]^{2+}$.

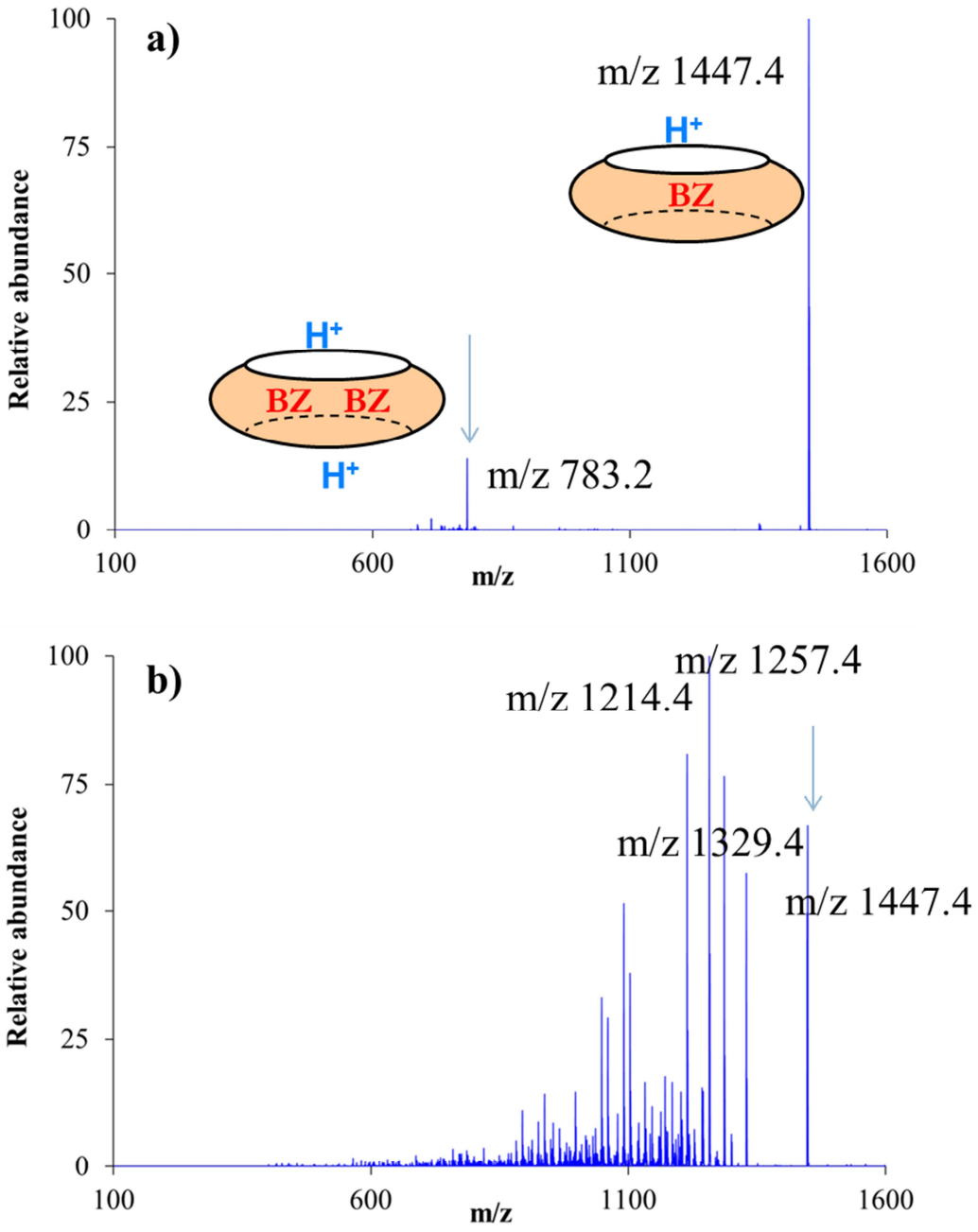

Figure S2. Fragmentation spectra of the ion at m/z 783.2. **a)** MS^2(783.2); **b)** MS^3(783.2→1447.4). Assignments: 783.2 $[CB8+2BZ+2H]^{2+}$; 1447.4 $[CB8+BZ+H]^{+}$; 1329.4 $[CB8+]^{+}$. The arrows indicate the fragmented peaks.

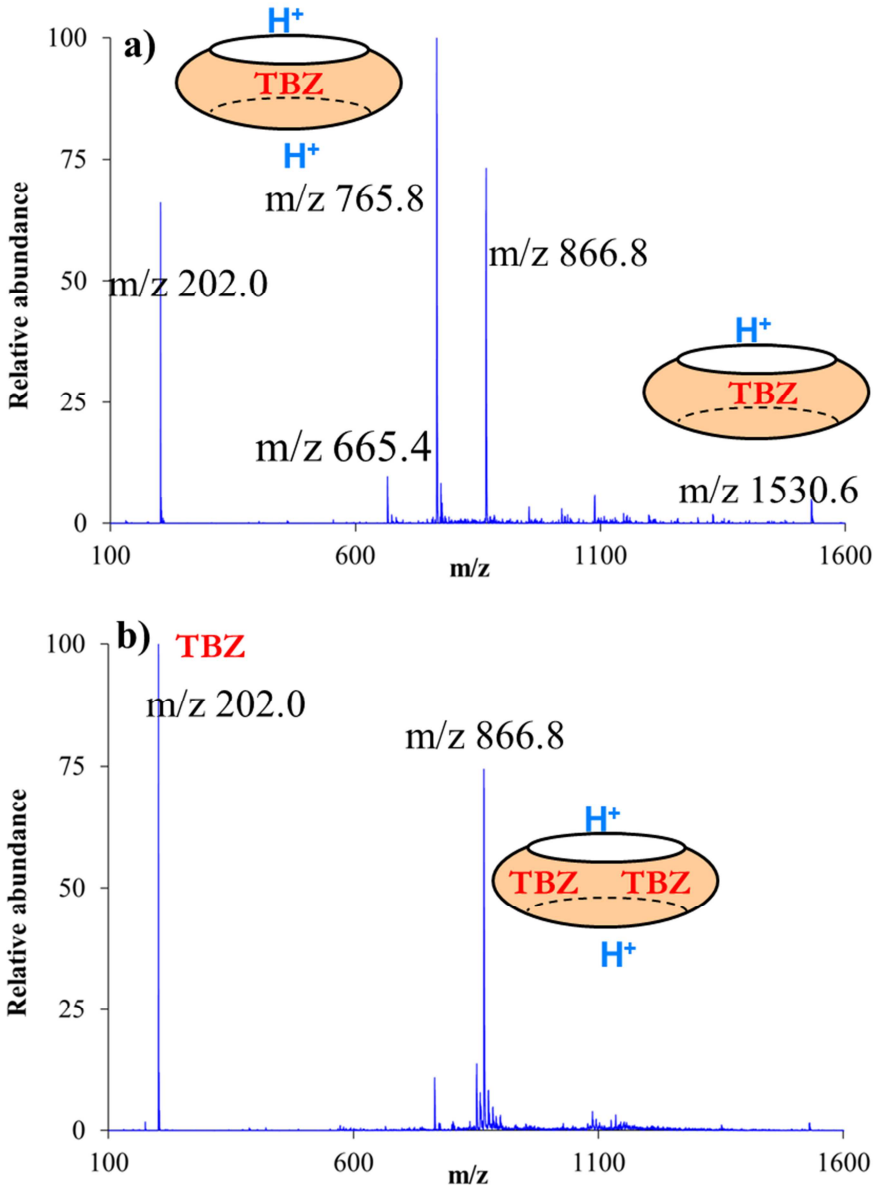

Figure S3. ESI-MS spectra (full scans) of aqueous solutions of TBZ and CB8 (1:1, stoichiometry) at pH ~ 6.5 (**a)** (30 μM) and pH 1.2 **(b))** (30 μM). Assignments: m/z 202.0 $[TBZ+H]^{+}$; 665.4 $[CB8+2H]^{2+}$; 765.8 $[CB8+TBZ+2H]^{2+}$; 866.8 $[CB8+2TBZ+2H]^{2+}$; 1530.6 $[CB8+TBZ+H]^{2+}$.

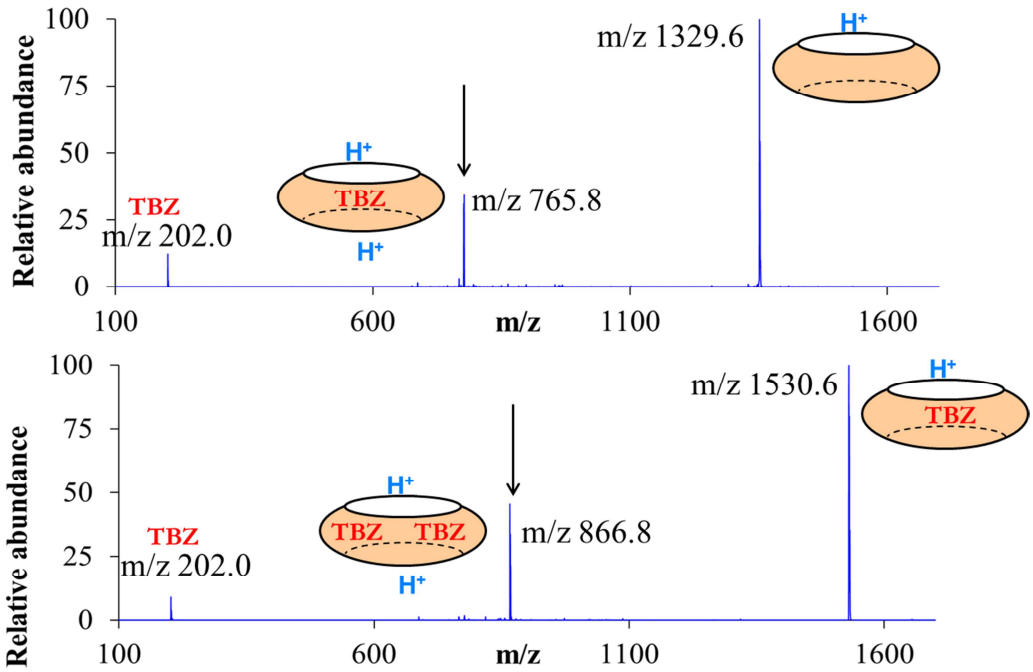

Figure S4. Fragmentation spectra (MS^2) of the ions at m/z 765.8 and 866.8. Assignments: m/z 202.0 $[TBZ+H]^+$; 765.8 $[CB8+TBZ+2H]^{2+}$; 1329.6 $[CB8+H]^+$, 866.8 $[CB8+2TBZ+2H]^{2+}$; 1530.6 $[CB8+TBZ+H]^+$. The arrows indicate the fragmented peaks.

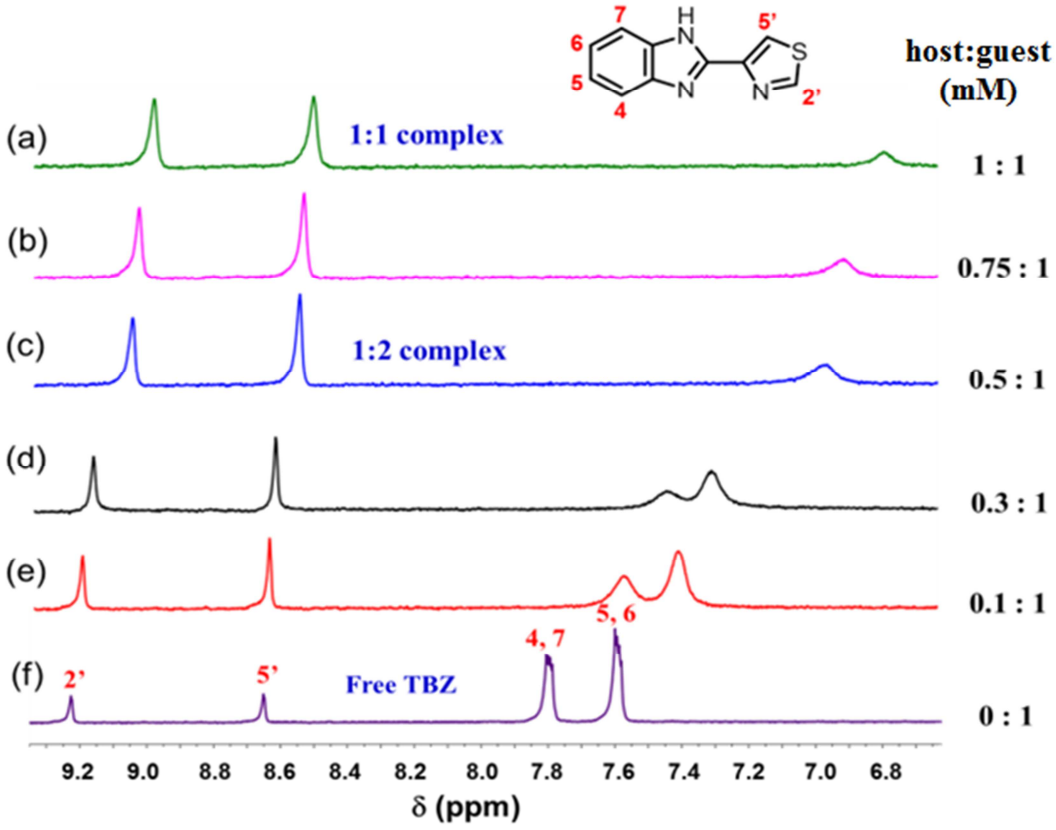

Figure S5. Partial 1H NMR spectra (D2O) of TBZ and TBZ-CB8 with different stoichiometries. [TBZ] = 1 mM. pH = 1.2.

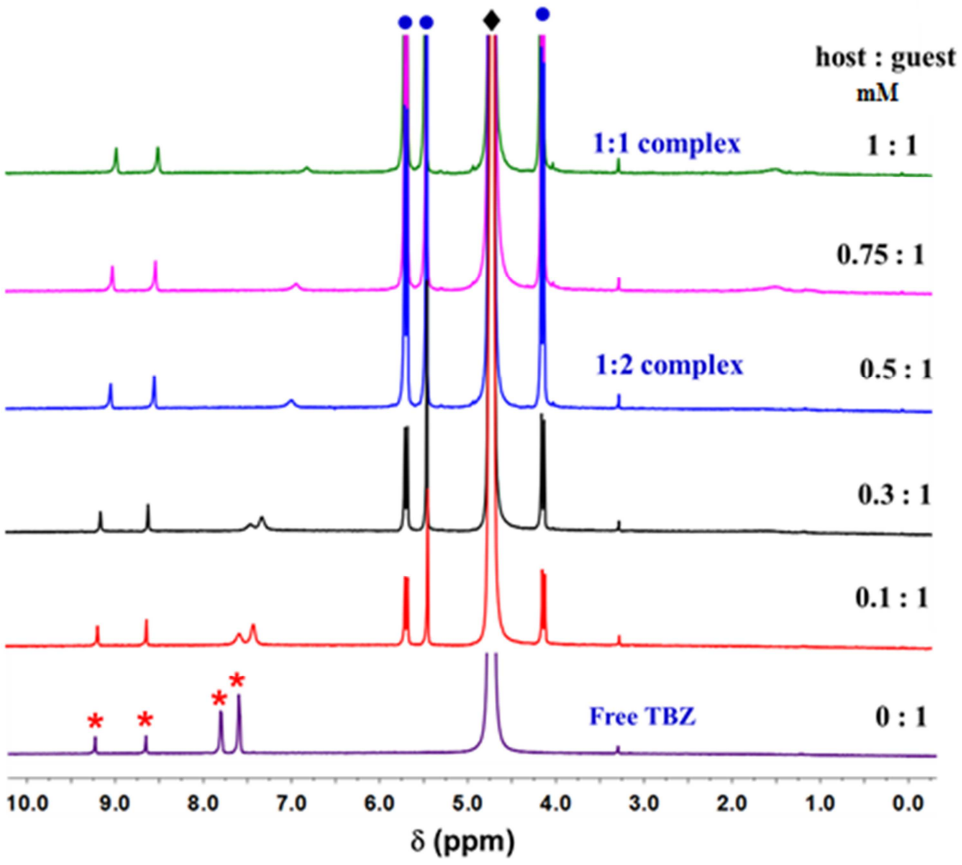

Figure S6. Full ^{1}H NMR spectra (500 MHz, D_2O) for the formations of 1:2 (Host: guest) and 1:1 (Host: guest) complexes for TBZ@CB8. [TBZ] = 1 mM, pH=1.2; the solution became turbid after addition of CB8 to the complex beyond TBZ : CB8 = 1:1 ratio indicating the completion of the complex formation. "*", "●" and "♦" represent the guest, host and residual H_2O signal respectively.

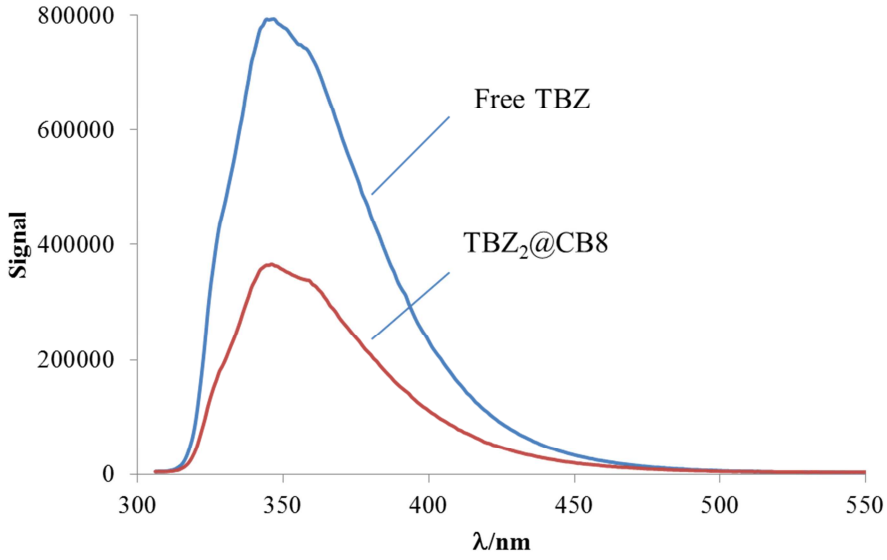

Figure S7. Steady state emission spectra of free TBZ and TBZ_2@CB8 (500 μM) at pH 1.2.

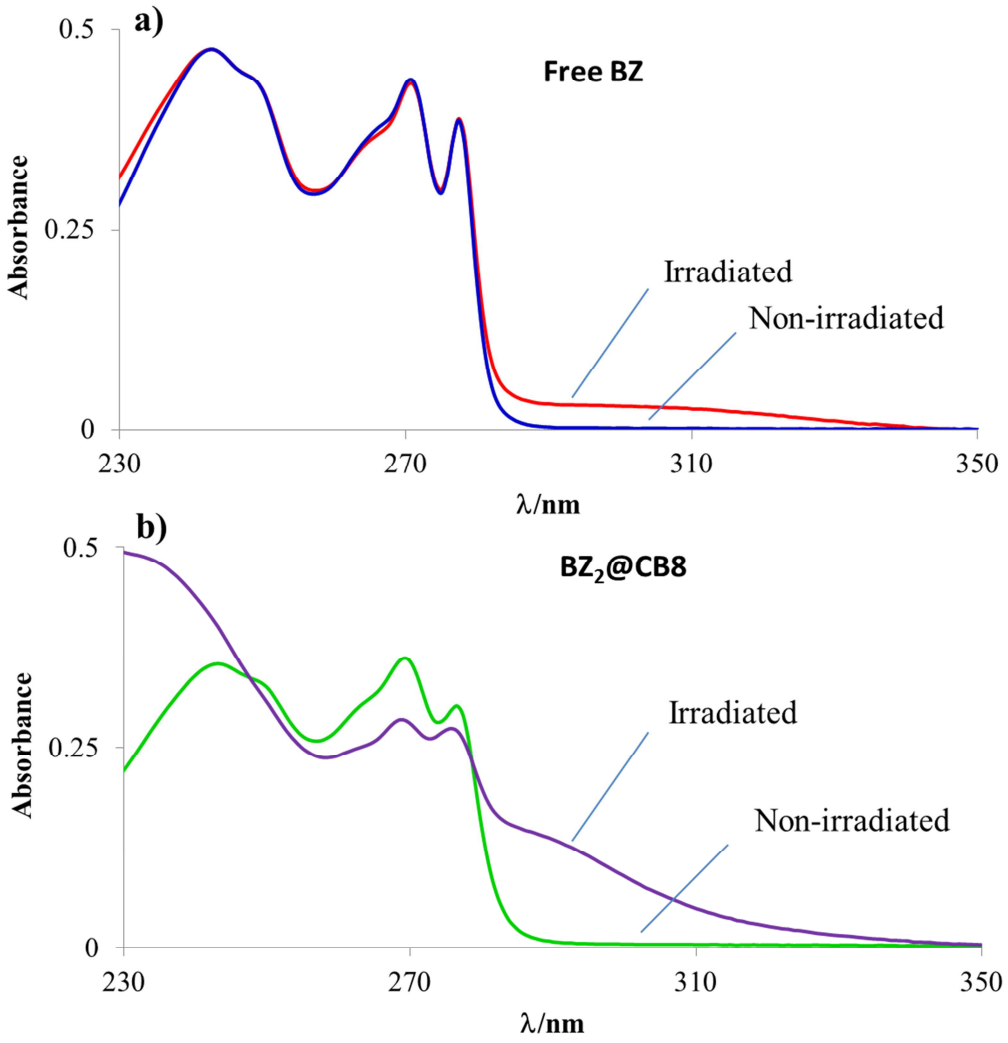

Figure S8. UV-Vis absorption spectra of BZ (**a)**) and BZ_2@CB8 (**b)**), before and after irradiation. The concentrations were 100 μM and 50 μM for BZ and CB8, respectively.

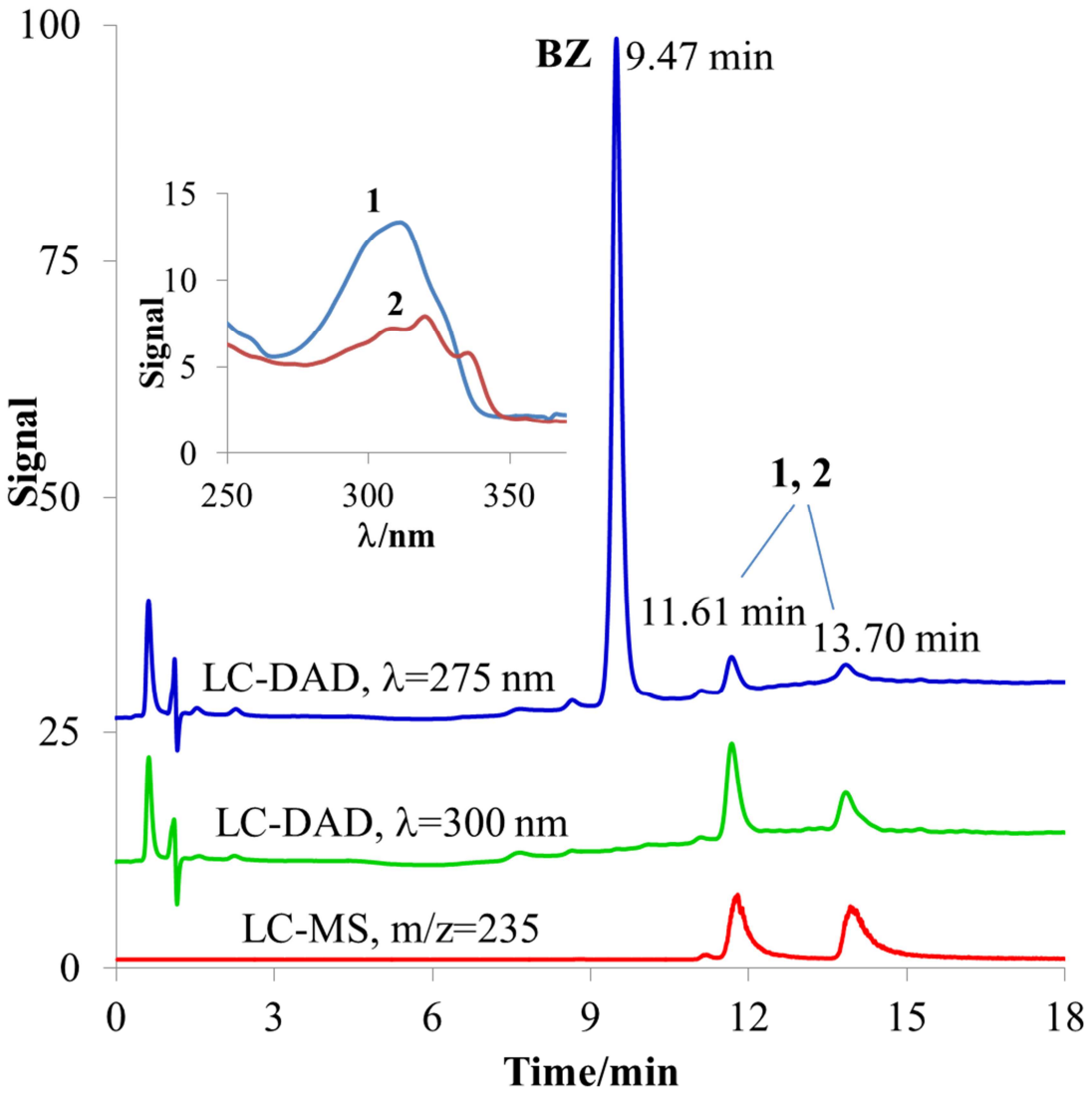

Figure S9. LC-DAD traces and LC-MS trace at m/z 235 of an irradiated aqueous solution with free BZ (100 μM) at pH 6.5. **1** and **2** are dehydrodimerization photoproducts. The inset shows the absorbance spectra of the photoproducts.

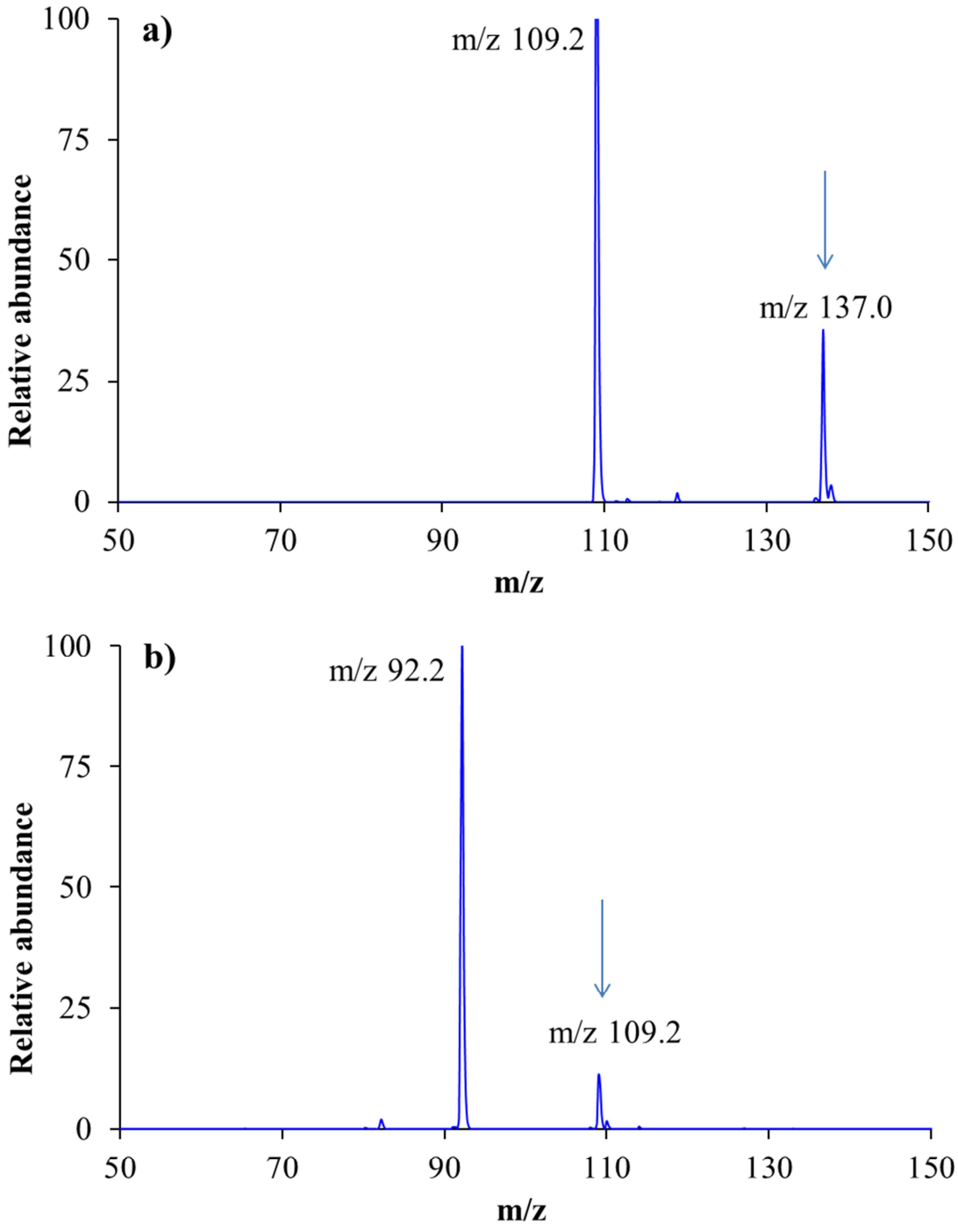

Figure S10. Fragmentation spectra of the ion at m/z 137.0. **a)** $MS^2(137.0)$; **b)** $MS^3(137.0 \rightarrow 109.2)$. The arrows indicate the fragmented peaks.

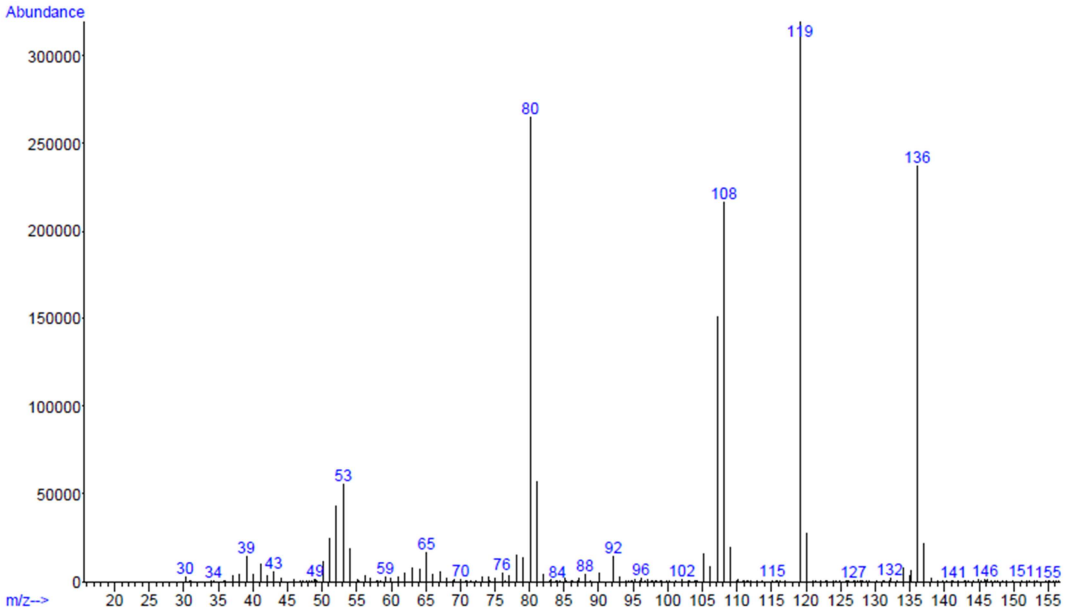

Figure S11. Mass spectrum (E.I.) of photoproduct of BZ_2@CB8.

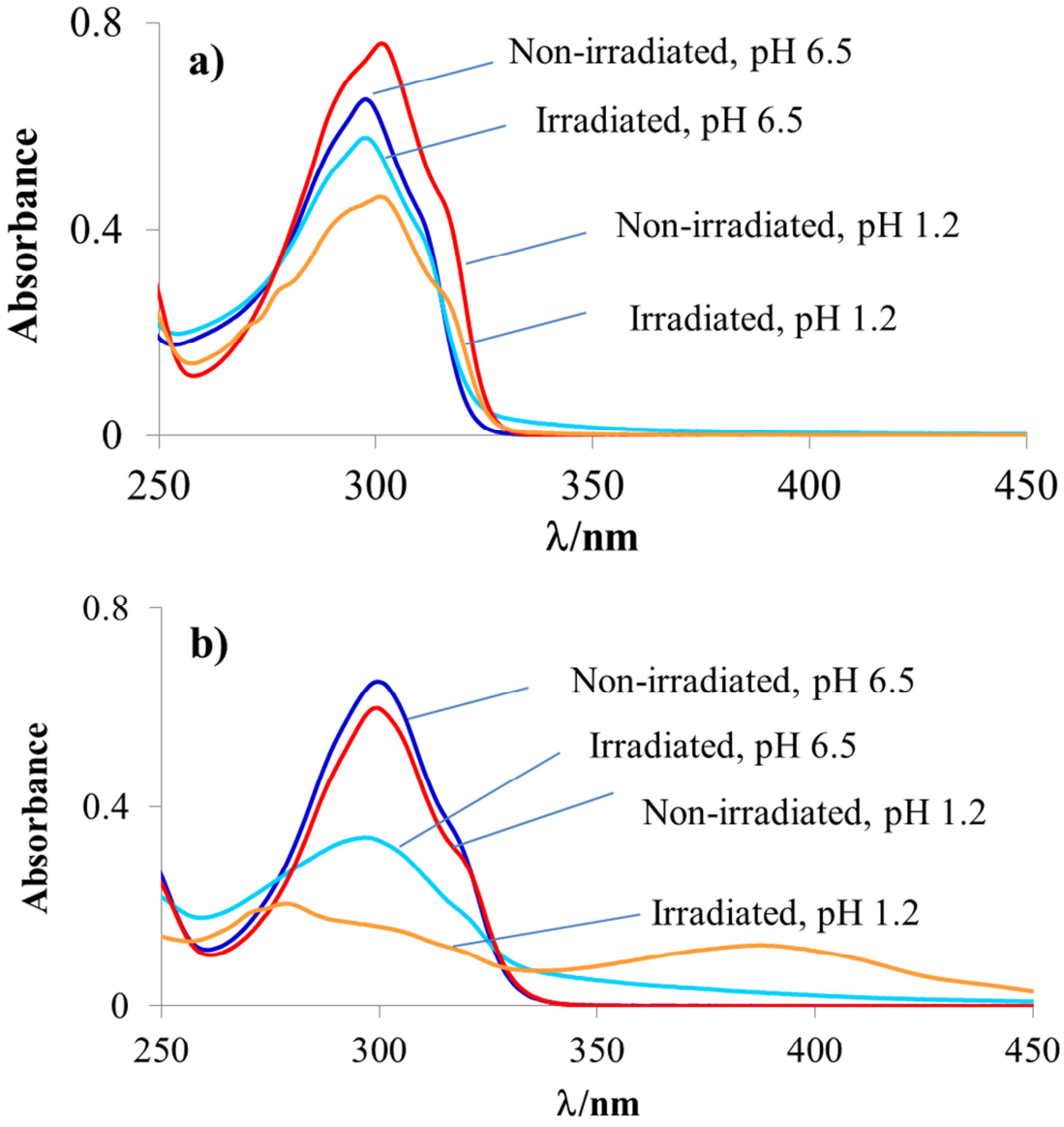

Figure S12. UV-Vis absorbance spectra of free TBZ, **a)**, and TBZ_2@CB8, **b)**, (~ 20 μM), before and after irradiation, at pH 6.5 and 1.2.

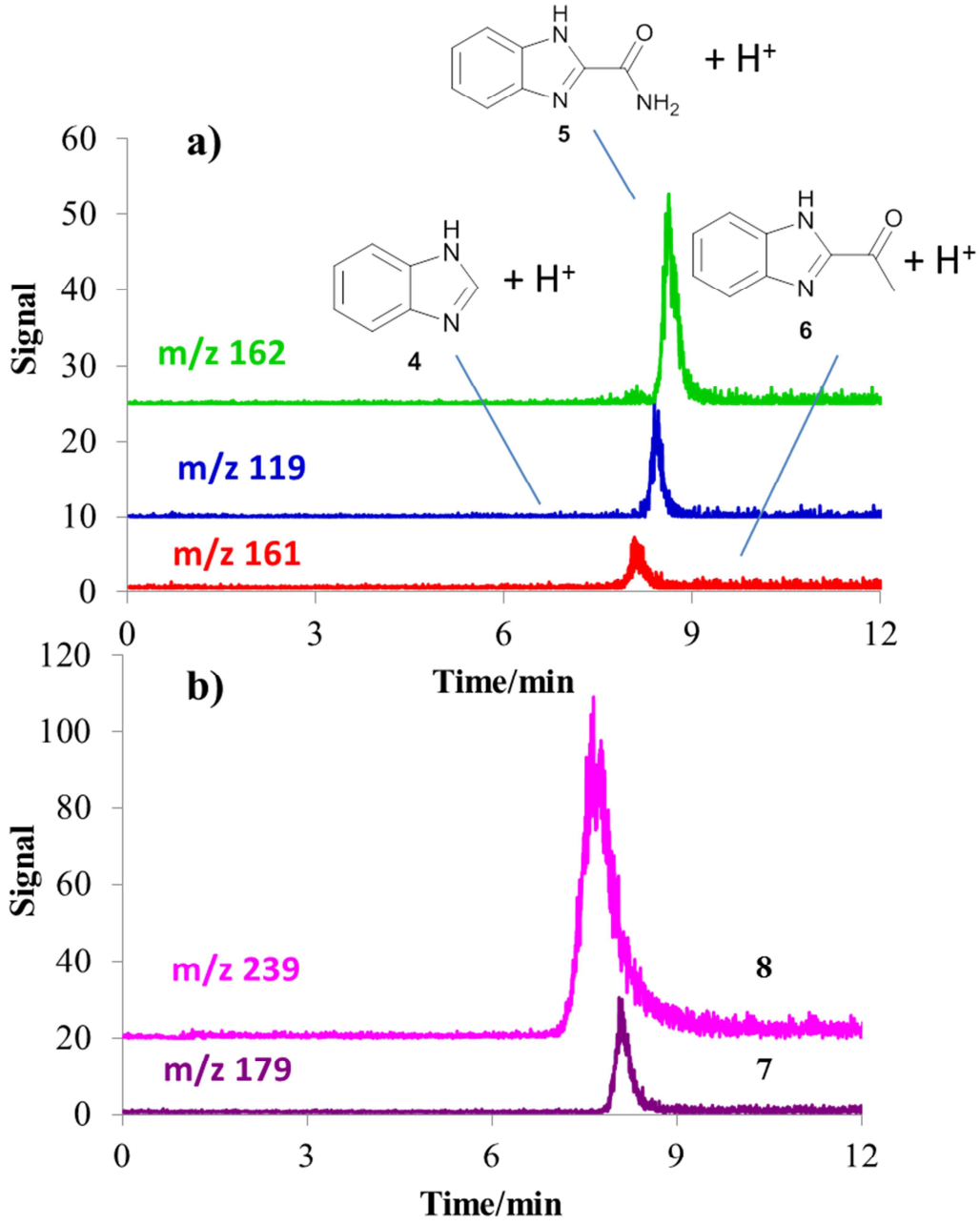

Figure S13. Single ion traces at m/z 119, 161, 162, 179 and 239 for an irradiated sample of free TBZ in aqueous solution at pH 1.2. The insets show the structures of the identified compounds. **7** and **8** are non-identified compounds.

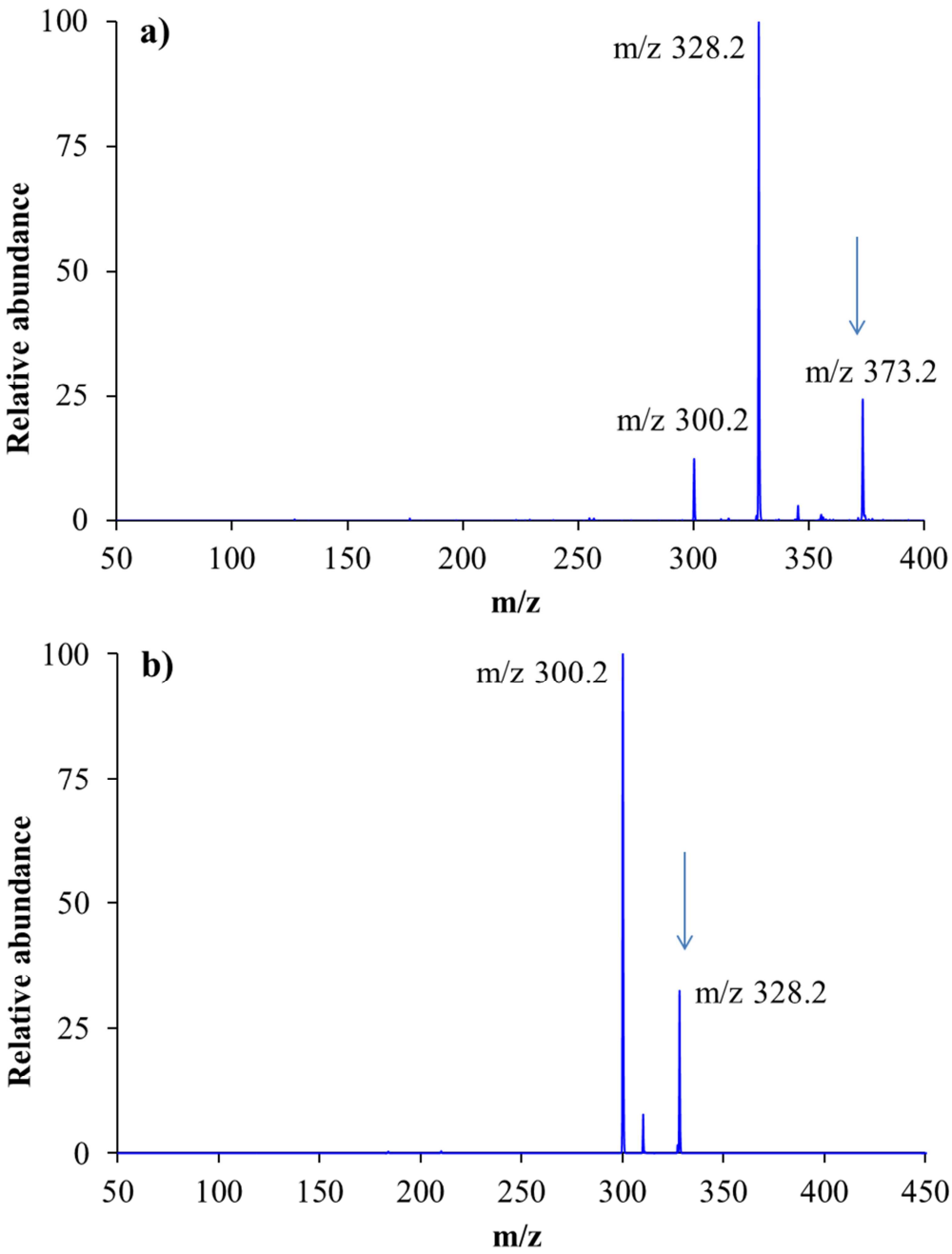

Figure S14. Fragmentation spectra of the ion at m/z 373.2. a) MS^2(373.2); b) MS^3(373.2→328.2). The arrows indicate the fragmented peaks.

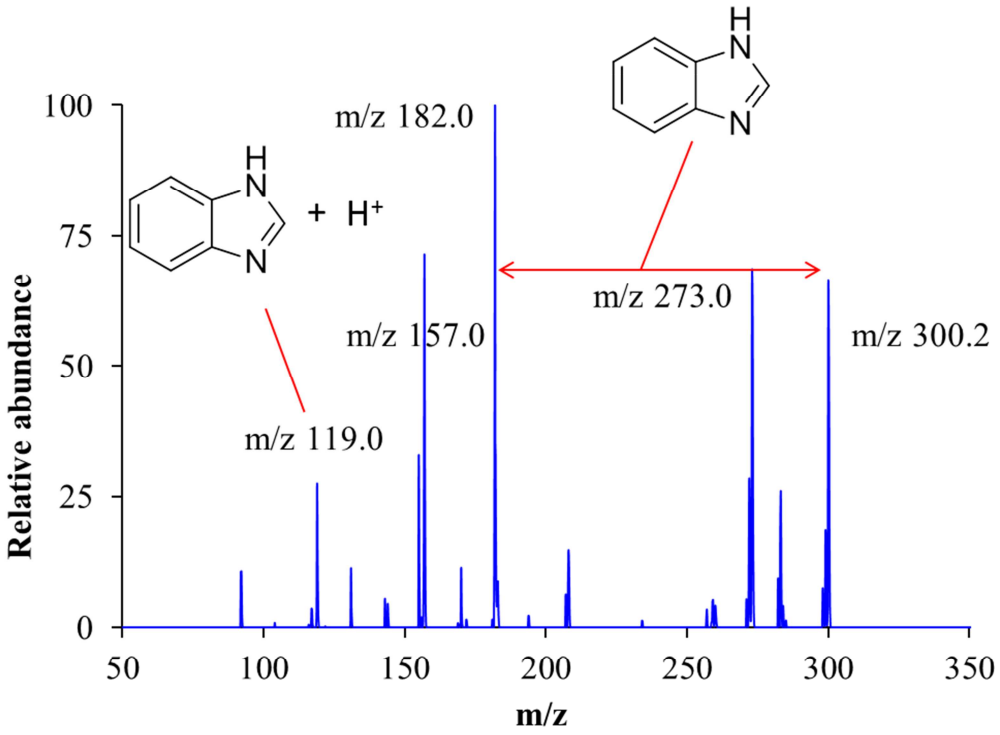

Figure S15. Fragmentation spectra of the ion at m/z 373.2 (MS^4(373.2→328.2→300.2)). The arrow indicates the fragmented peak. The insets show the structure of the ion at m/z 119.0 and the neutral loss that gives m/z 182.0

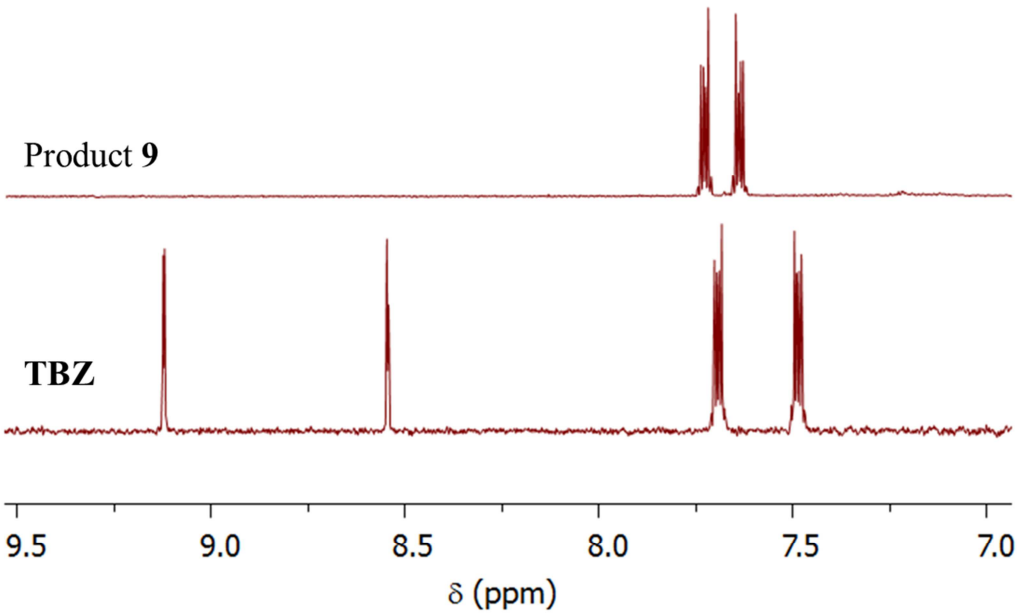

Figure S16. Detail of the ^{1}H NMR spectra of TBZ and of photoproduct **9**.