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SUPPLEMENTARY MATERIAL

Barrierless Reactions of Three Benzonitrile Radical Cations with Ethylene

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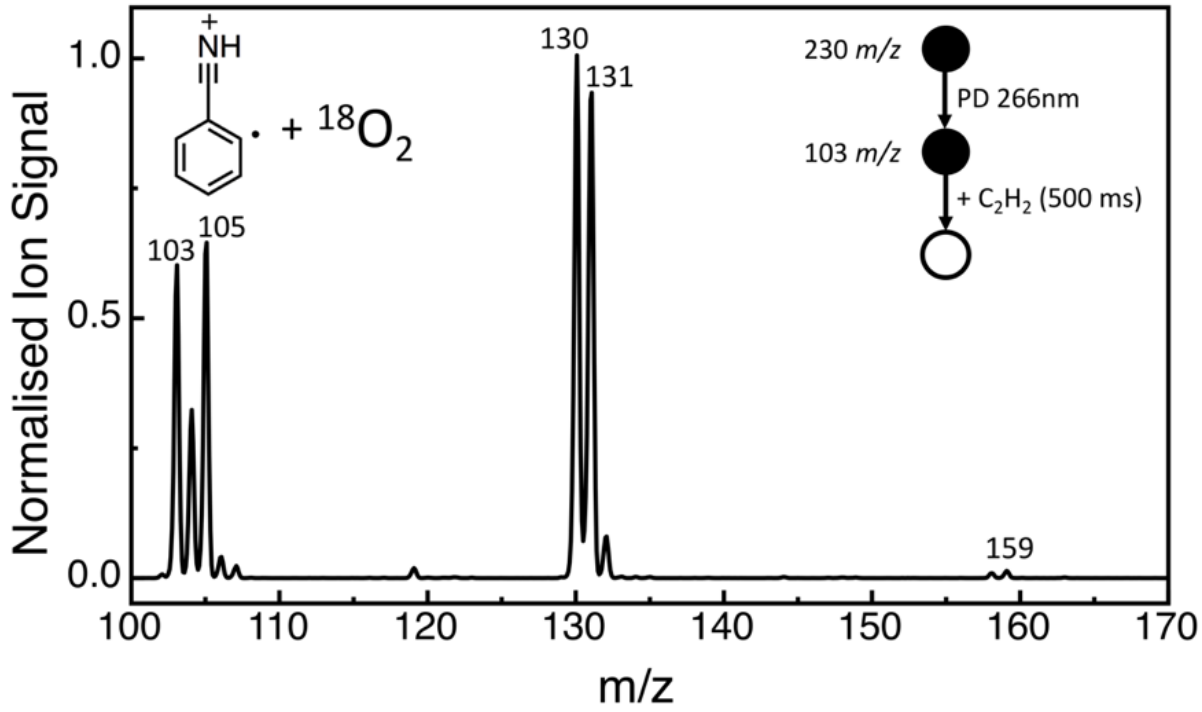

Fig. S1: Product mass spectrum for the reaction of 2DBz + ethylene in the presence of $^{18}O_2$, averaged from 500 individual mass spectra. The additional product mass channel at *m/z* 105 suggests the formation of a dehydrobenzaldehyde radical cation through an oxygen addition mechanism *via* the loss of $H_2N^{18}O$. The same reaction with ambient oxygen will instead lead to the formation of signal at *m/z* 103, which is the same *m/z* value as the dehydrobenzonitrilium radical cation. The regeneration of signal at *m/z* 103 will produce the biexponential kinetics seen for the reaction of ethylene + dehydrobenzonitrilium. Similarly, a minor product peak is also observed at *m/z* 106, possibly indicating *m/z* 104 corresponds to an oxygen addition product.

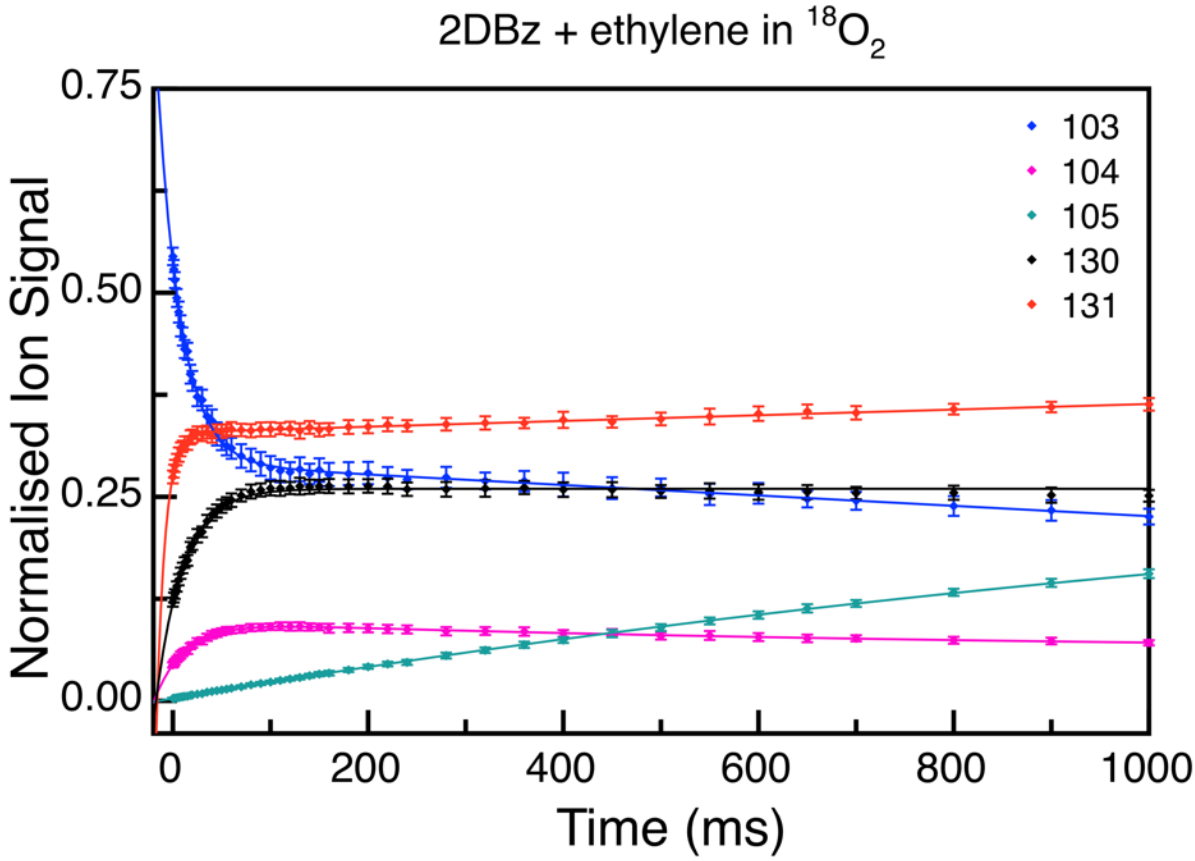

Fig. S2: Kinetic profiles for the reaction of 2DBz + ethylene in the presence of $^{18}O_2$. Error bars represent 2σ. The growth of *m/z* 105 matches well with the slower decay of *m/z* 103, supporting the assignment of oxygen-mediated regeneration of signal at *m/z* 103.

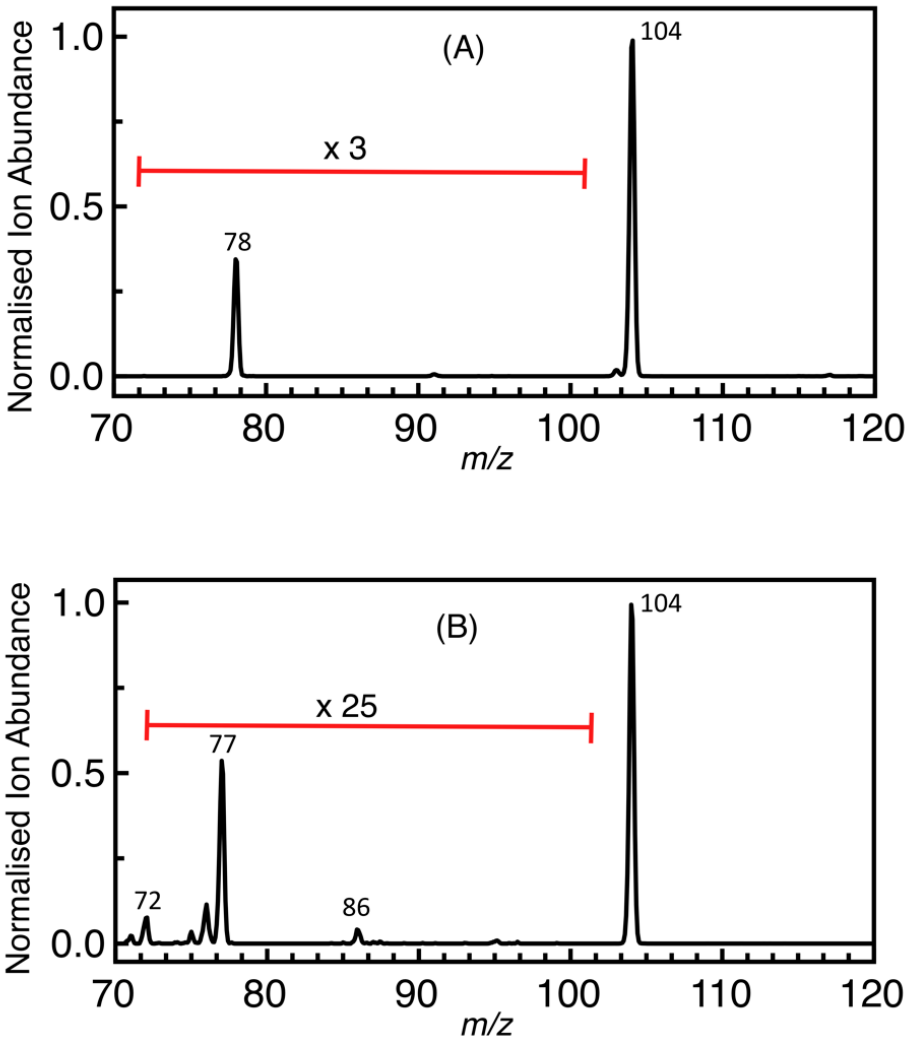

Fig. S3: CID mass spectra for the product ion at *m/z* 104 (A) and benzonitrileH$^+$ (B). Each mass spectrum is an average of 1000 individual mass spectra. *m/z* 104 was generated during reactions of 2DBz + ethylene and isolated after 500 ms of reaction. CID of the *m/z* 104 product leads to a loss of 26 Da, producing *m/z* 78, while CID of benzonitrileH$^+$ produces several new product signals at *m/z* 72, *m/z* 76, *m/z* 77 and *m/z* 86. The distinct difference between these two CID mass spectra support the assignment that the majority of 104 is not produced via H-atom abstraction of the dehydrobenzonitrilium radical cation, which would lead to the formation of benzonitrileH$^+$.