

SUPPLEMENTARY INFORMATION

Modelling Reaction Kinetics of Distonic Radical Ions: A Systematic Investigation of Phenyl-type Radical Addition to Unsaturated Hydrocarbons

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Figure S1 shows a representative mass spectrum, kinetic trace and *pseudo*-first order rate coefficient vs ethylene concentration plot to determine the second-order rate coefficient for the reaction of 4-dehydro-3-fluoropyridinium and ethylene.

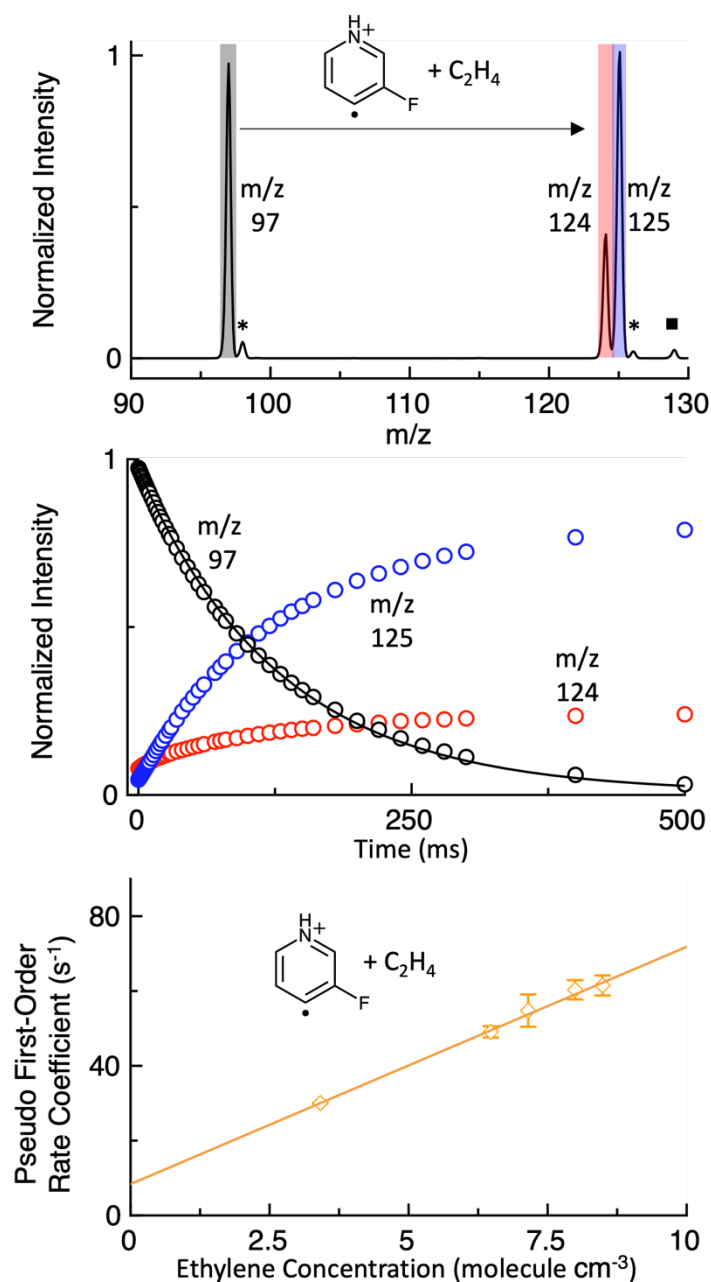


Figure S1: Representative plots of mass spectrum, reaction kinetics and *pseudo*-first order rate coefficients vs ethylene concentration plot for the reaction of 4-dehydro-3-fluoropyridinium + ethylene. Error bars represent 2σ . Asterisks denote products corresponding to H-atom abstraction, while ■ denotes products arising from competing reactions with background O_2 .

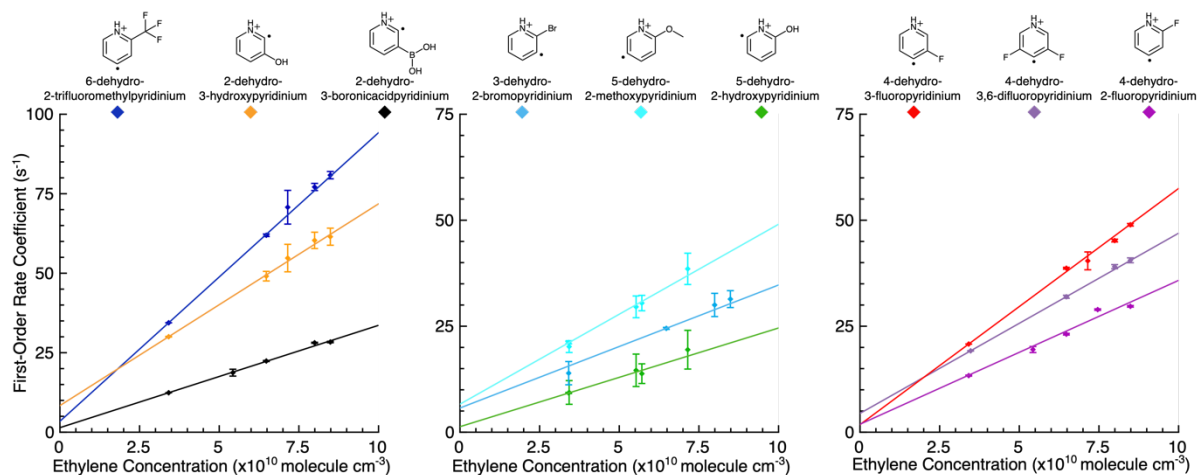


Figure S2. Plot of experimentally measured *pseudo*-first order rate coefficient vs ethylene concentration for each of the nine distonic ion-molecule reactions of this paper. Each dataset is grouped based on the location of the radical site relative to the charge (*ortho*, *meta* or *para*) and is fitted with a linear regression as shown by the solid line to derive the second-order rate coefficient for the reaction. Structures and names of the substituted pyridinium radical cations measured in this study are included in the legend below each plot.

Figure S2 displays *pseudo*-first order rate coefficient vs ethylene concentration plots used to extract the measured second-order rate coefficient for each of the nine ethylene-addition distonic ion-molecule reactions reported for the first time in this paper. The structure of each of these nine substituted pyridines are included in the legend of this plot. Each radical cation is group based on the position of the radical site, either *ortho*, *meta* or *para* to the charge centre, however, unsurprisingly it is clear from this figure that there is no clear correlation between the radical position and the reaction rate.