

SUPPORTING INFORMATION

Detection of Transient Radical Cations in Electron Transfer Initiated Diels-Alder Reactions by Electrospray Ionization Mass Spectrometry

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Reaction of phenylvinylsulfide and cyclopentadiene:

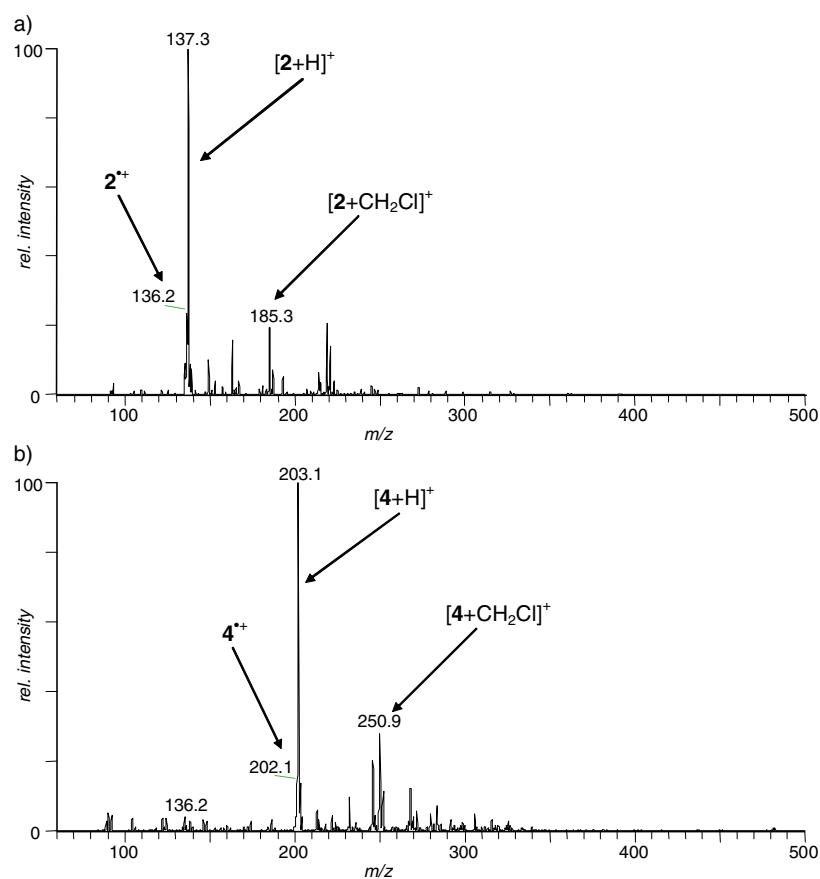


Figure S1. a) Positive APCI mass spectrum of a solution of phenylvinylsulfide (**2**) in dichloromethane.

b) Positive APCI mass spectrum of a solution of 5-(phenylthio)norbornene (**4**) in dichloromethane.

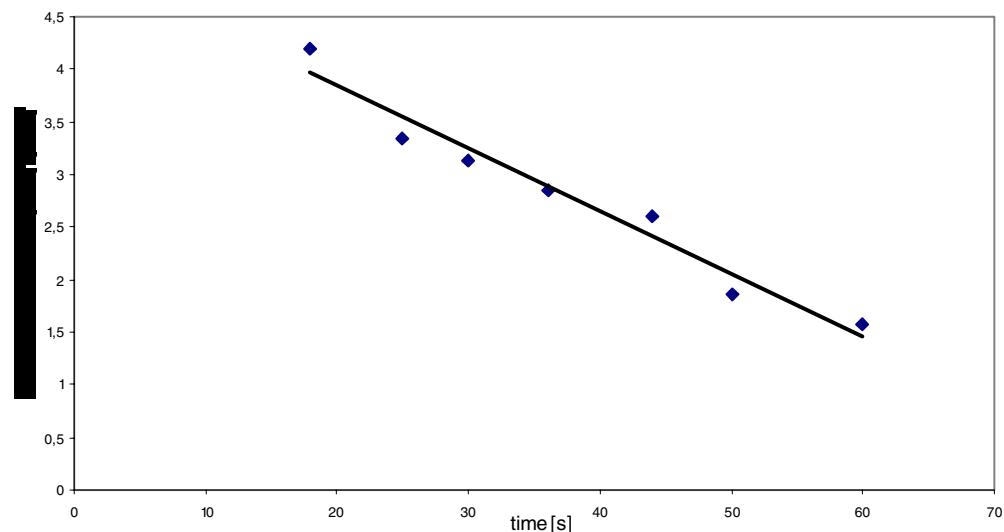


Figure S2. APCI-MS investigation of the tris(*p*-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^+\text{SbCl}_6^-$) initiated Diels-Alder reaction of phenylvinylsulfide (**2**) and cyclopentadiene

(3) to 5-(phenylthio)norbornene (**4**). Ratio of the intensities of the protonated substrate $[2+\text{H}]^+$ (m/z 137) and protonated product $[4+\text{H}]^+$ (m/z 203) vs. reaction time.

Reaction of *trans*-anethole and isoprene:

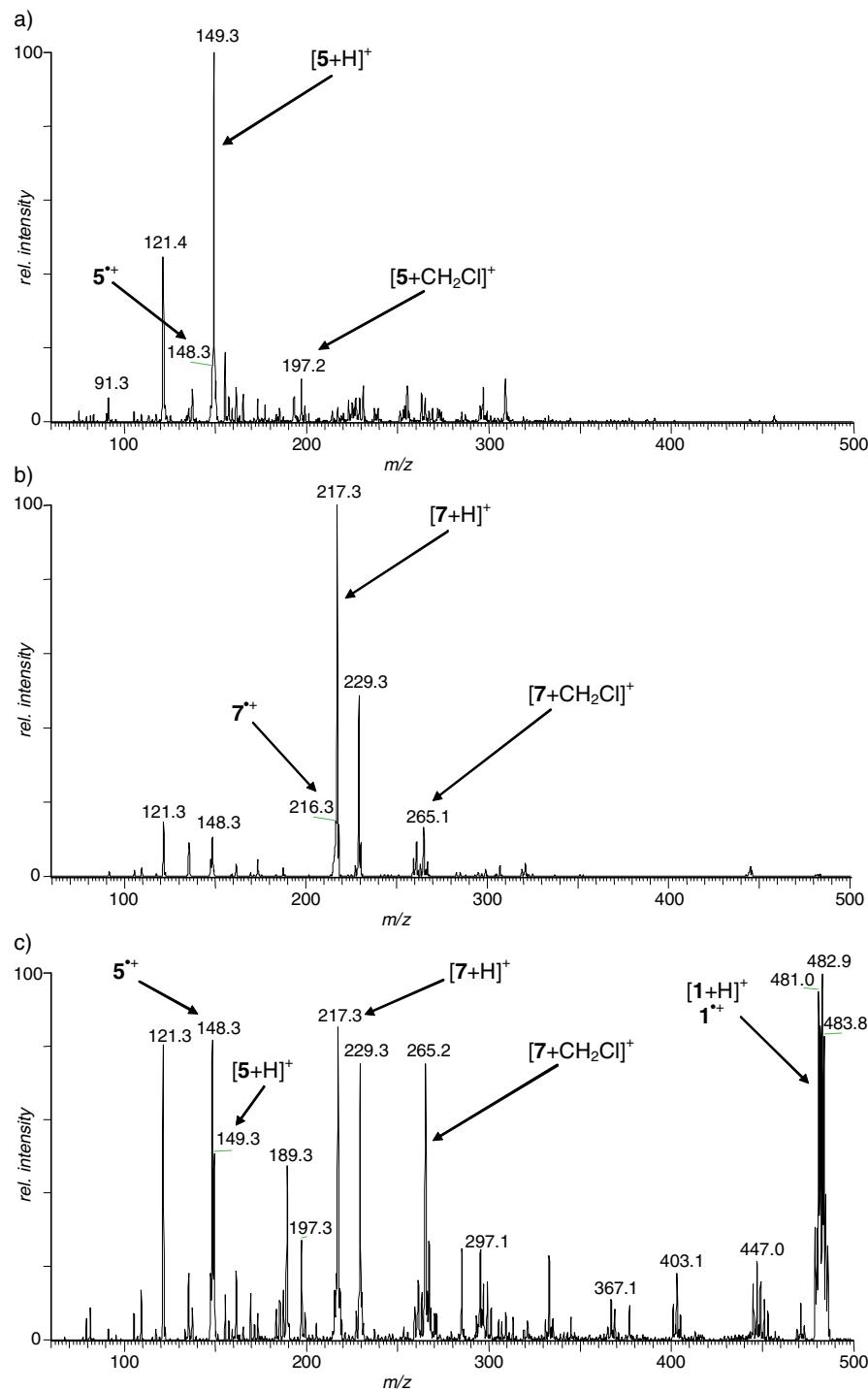


Figure S3. a) Positive APCI mass spectrum of a solution of *trans*-anethole (**5**) and isoprene (**6**) in dichloromethane.

b) Positive APCI mass spectrum of a solution of *trans*-1,5-dimethyl-4-(4'-methoxyphenyl)-cyclohexene (**7**) in dichloromethane.

c) Positive APCI mass spectrum of the reacting solution of *trans*-anethole (**5**), isoprene (**6**) and tris(*p*-bromophenyl)aminium hexachloroantimonate (**1**⁺SbCl₆⁻) in dichloromethane after approximately 10 s reaction time.

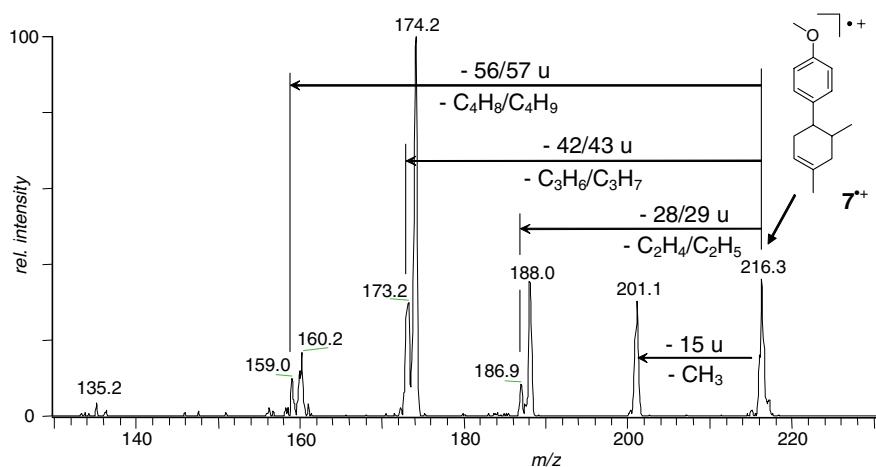


Figure S4. APCI-MS/MS spectrum of the molecular ion of *trans*-1,5-dimethyl-4-(4'-methoxyphenyl)-cyclohexene **7**⁺ (m/z 216).

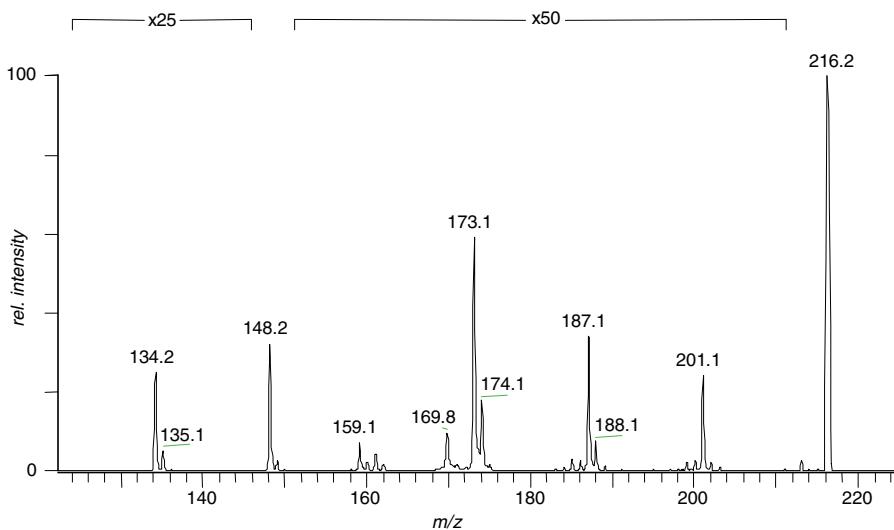


Figure S5. CID-Mass spectrum of EI generated parent ion of *trans*-1,5-dimethyl-4-(4'-methoxyphenyl)-cyclohexene **7**⁺ (m/z 216). 25 and 50 fold zoomed in the mass range of m/z 120 to m/z 210.

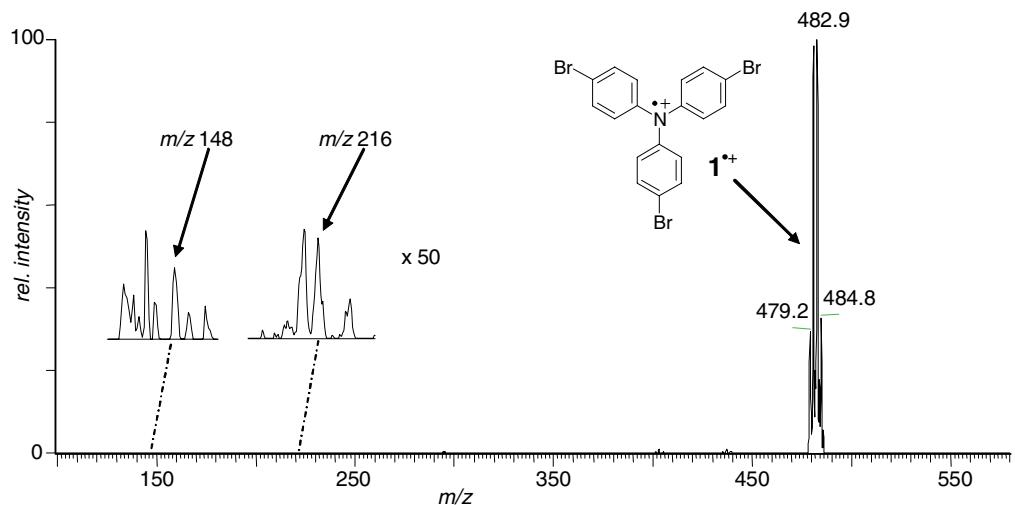


Figure S6. Positive ESI mass spectrum of the reacting solution of *trans*-anethole (**5**), isoprene (**6**) and aminium salt $\mathbf{1}^+\text{SbCl}_6^-$ in dichloromethane after a reaction time of approximately 7 seconds.

Dimerization of 1,3-cyclohexadiene:

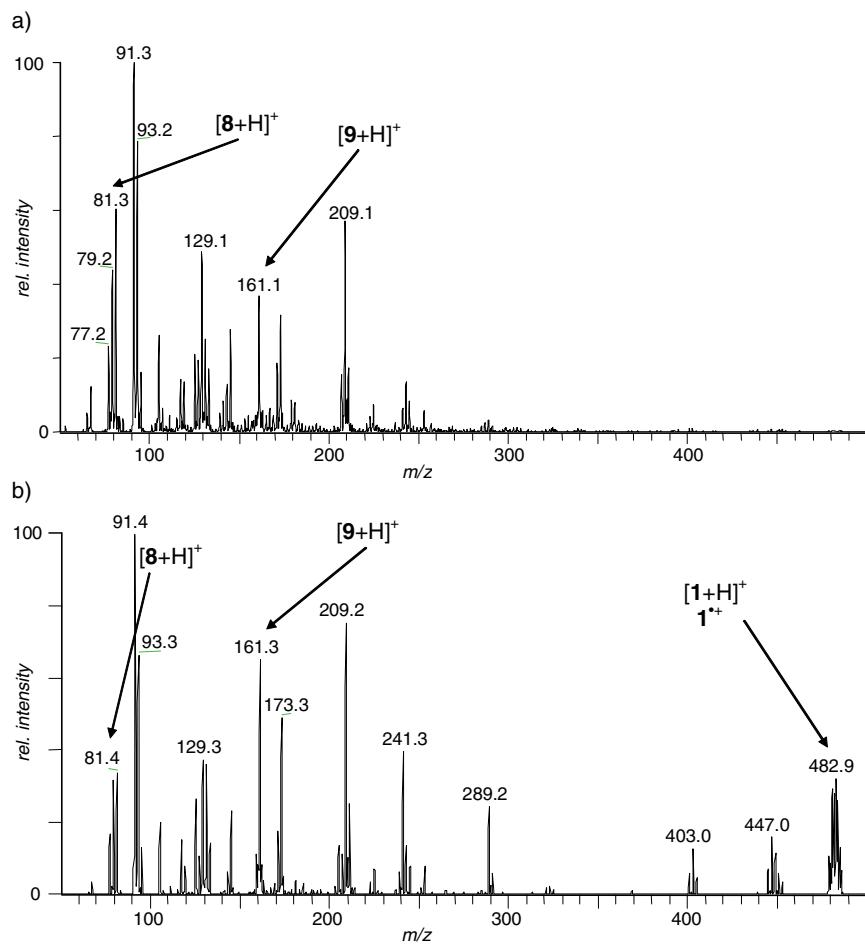


Figure S7. a) Positive APCI mass spectrum of a solution of cyclohexadiene (**8**) in dichloromethane.

b) Positive APCI mass spectrum of the reacting solution of cyclohexadiene (**8**) and aminium salt $\mathbf{1}^+\text{SbCl}_6^-$ in dichloromethane after approximately 10 s reaction time.

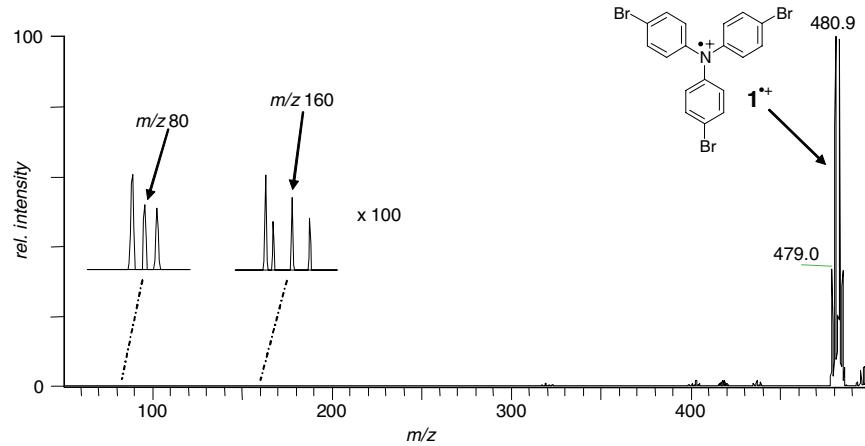


Figure S8. Positive ESI mass spectrum of the reacting solution of cyclohexadiene (**8**) and aminium salt $\mathbf{1}^+\text{SbCl}_6^-$ in dichloromethane after a reaction time of approximately 7 seconds.

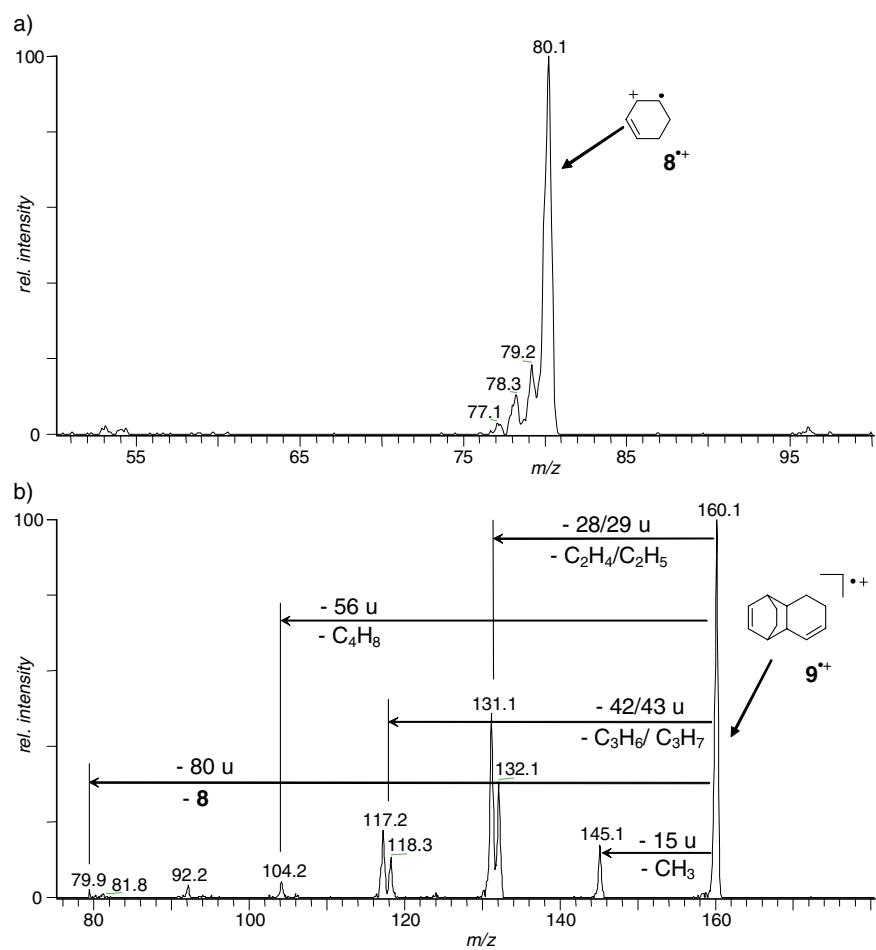


Figure S9. a) APCI-MS/MS spectrum of the molecular ion of cyclohexadiene $\mathbf{8}^{\bullet+}$ (m/z 80).

b) APCI-MS/MS spectrum of the molecular ion of the cyclohexadiene dimer $\mathbf{9}^{\bullet+}$ (m/z 160).