Supporting Information

Figure S1. CID spectrum of $[GGR–OMe + H]^+$.

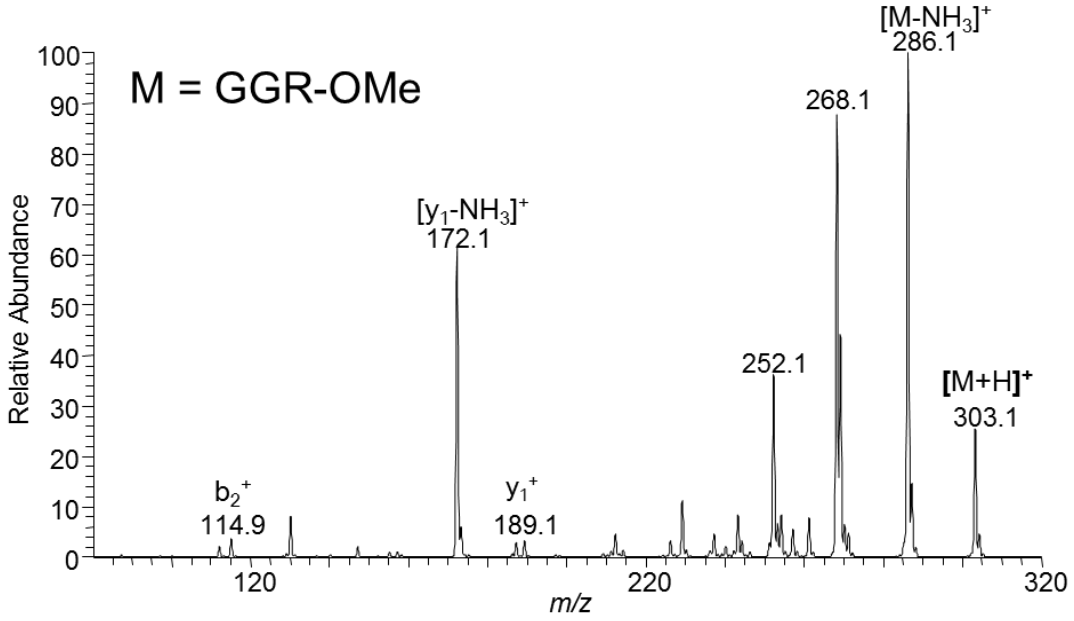
Figure S2. Potential energy surface of $[a_3 + H]^{\bullet+}$ (CO_2 loss) generated from $[GG^{\bullet}R]^+$. The upper numbers are enthalpies at 0 K; the lower italicized numbers are free energies at 298 K. All energies (in kcal mol^{-1}) are provided relative to $[G^{\bullet}GR]^+$-1, which is the global minimum of $[G^{\bullet}GR]^+$. Selective bond lengths are in Å.

Figure S3. Potential energy surface of y_1^+ generated from $[G^{\bullet}GR]^+$ through the pathway involving an anhydride intermediate. The upper numbers are enthalpies at 0 K; the lower italicized numbers are free energies at 298 K. All energies (in kcal mol^{-1}) are provided relative to $[G^{\bullet}GR]^+$-1, which is the global minimum of $[G^{\bullet}GR]^+$. Selective bond lengths are in Å.

Figure S4. Key transition state for the y_2^+ generated from $[G^{\bullet}GR]^+$ via a pathway involving anhydride intermediate.

Figure S5. Key transition state for the isomerization from $[G^{\bullet}GR]^+$ to $[GGR_{\gamma}^{\bullet}]^+$.

17 **Figure S1**



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20 **Figure S2**

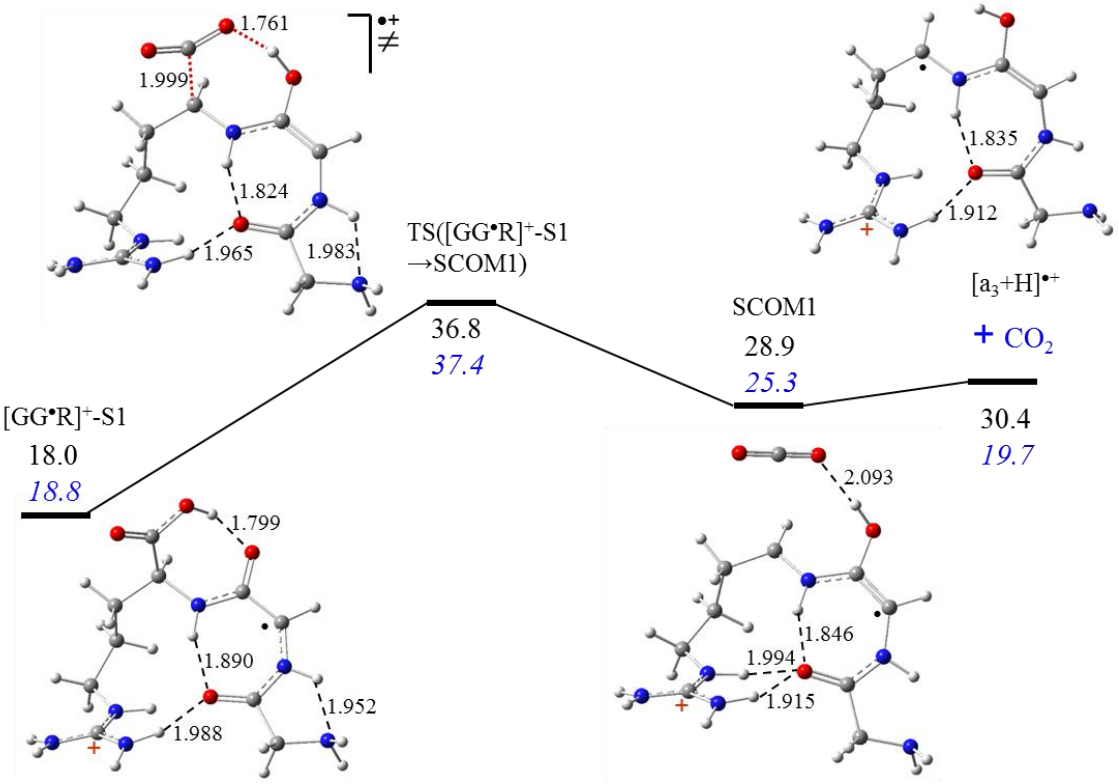

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Figure S3

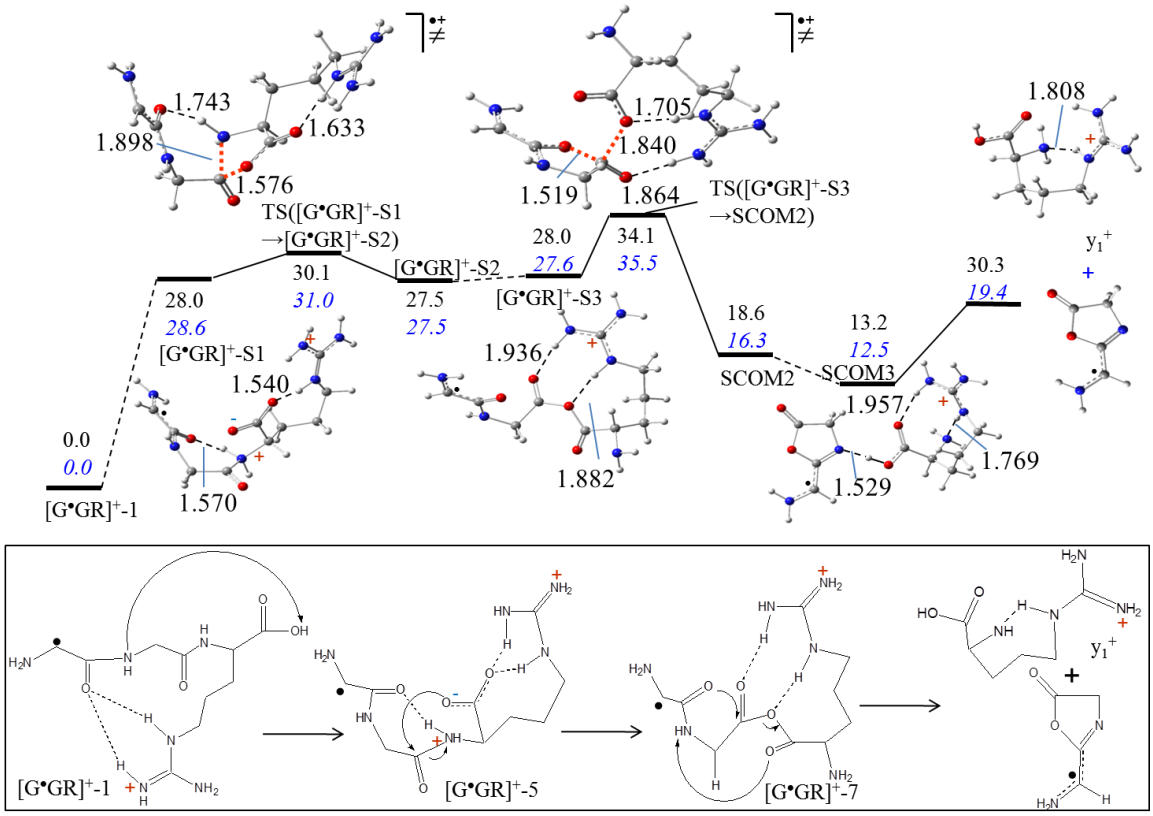
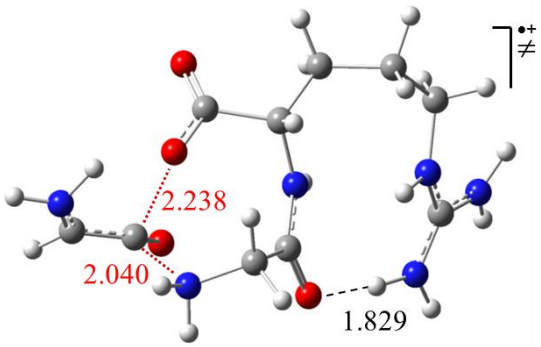


Figure S4

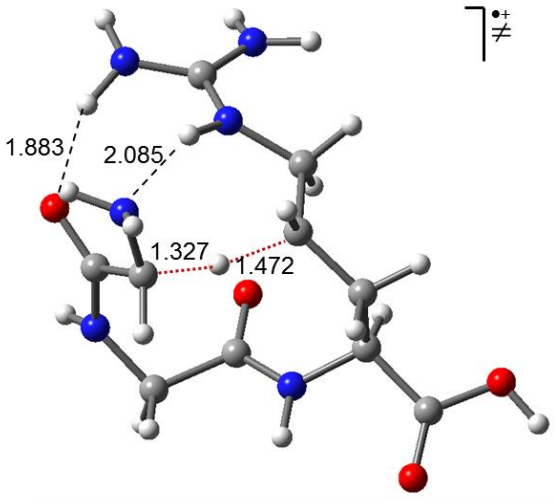


Alternative TS of formation of y_2^+ from $[G•GR]^+$

ΔH_0^o = 63.7 kcal mol^{-1}

ΔG_{298}^o = 64.8 kcal mol^{-1}

31 **Figure S5**



TS-[G$^{\bullet}$GR]$^{+}$→[GGR$_{\gamma}^{\bullet}$]$^{+}$

ΔH_0^o = 42.0 kcal mol^{-1}

ΔG_{298}^o = 45.0 kcal mol^{-1}

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