

**Nucleophilic substitution by amide nitrogen in the aromatic rings of  
[z<sub>n</sub> – H]<sup>++</sup> ions; the structures of the [b<sub>2</sub> – H – 17]<sup>++</sup> and [c<sub>1</sub> – 17]<sup>+</sup> ions**

*Xiaoyan Mu,<sup>a</sup> Justin Kai-Chi Lau,<sup>b,c</sup> Cheuk-Kuen Lai,<sup>a</sup> K.W. Michael Siu,<sup>b,c</sup>*

*Alan C. Hopkinson,<sup>b\*</sup> Ivan K. Chu<sup>a\*</sup>*

*<sup>a</sup>Department of Chemistry, The University of Hong Kong, Hong Kong, China.*

*<sup>b</sup>Department of Chemistry and Centre for Research in Mass Spectrometry, York University, 4700  
Keele Street, Toronto ON, Canada M3J 1P3*

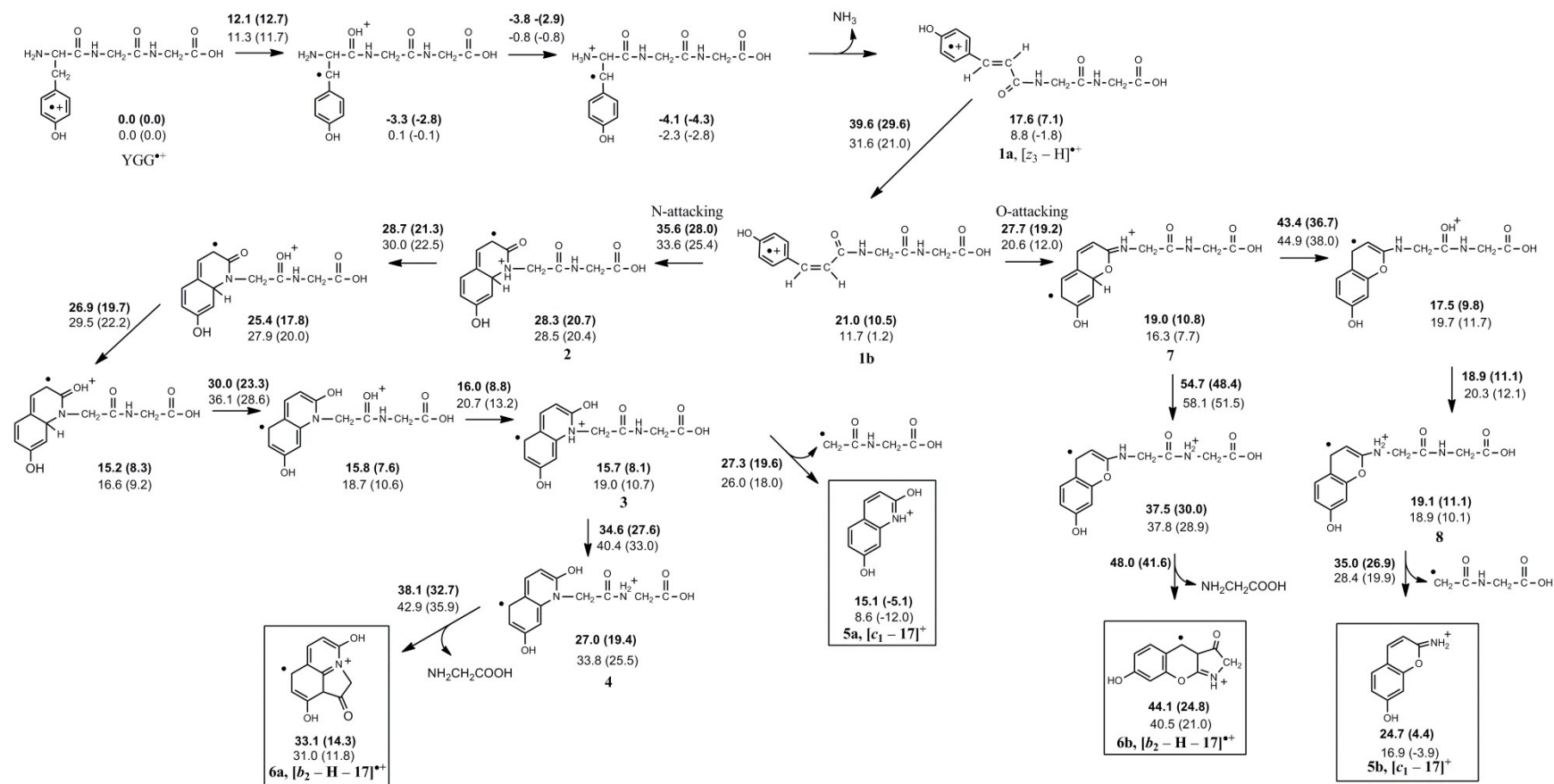
*<sup>c</sup>Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue,  
Windsor, ON, Canada N9B 3P4*

**Supplementary Materials**

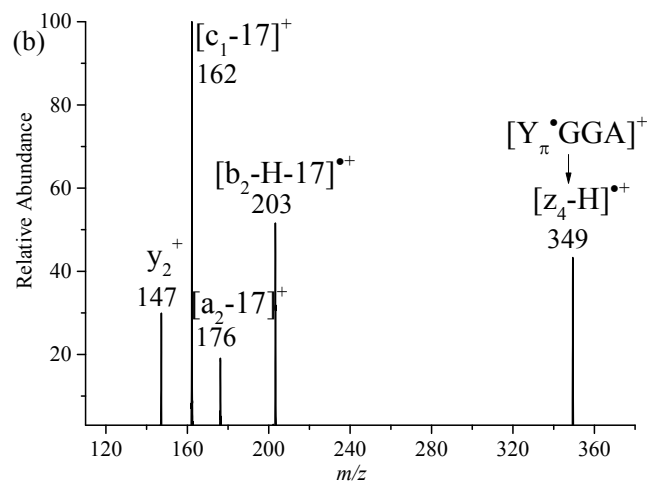
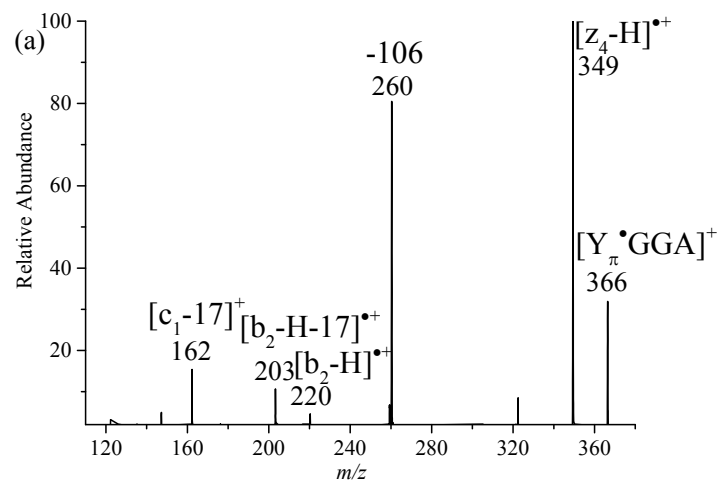
\*Corresponding authors

Email: ach@yorku.ca; ivankchu@hku.hk

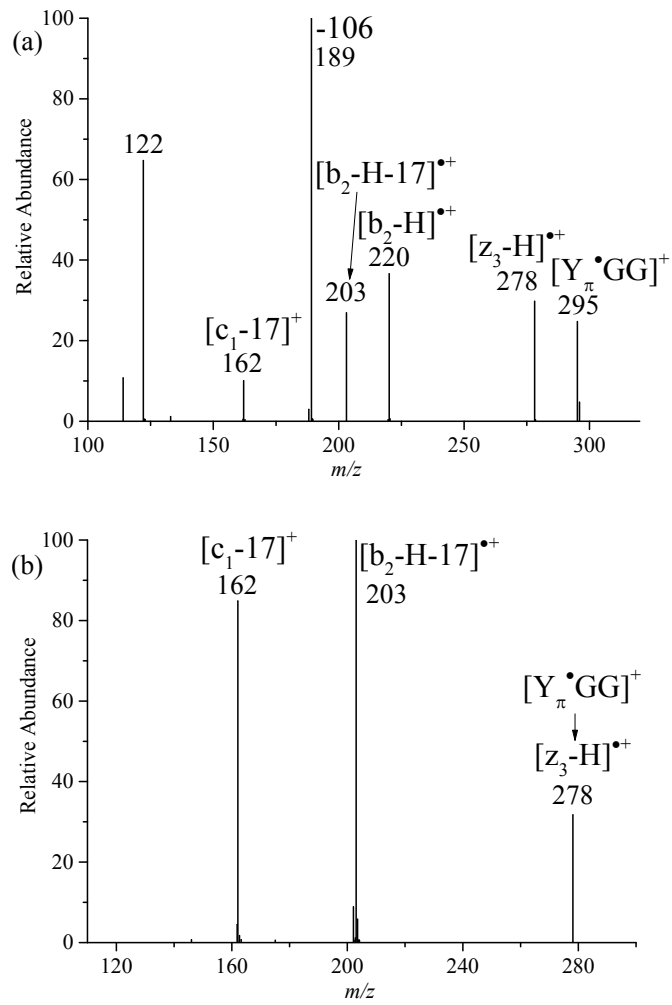
**Scheme S1** Detailed mechanism showing the formations of  $[c_1 - 17]^+$  and  $[b_2 - H - 17]^+$  ions from  $[YGG]^+$  via nucleophilic attack by backbone nitrogen or oxygen. Upper numbers are the relative enthalpies ( $\Delta H^0$ ) and free energies ( $\Delta G^0_{298}$ , in parenthesis) calculated at M062X/6-31++G(d,p) level while the lower numbers are those calculated at the B3LYP/6-31++G(d,p) level. All energies are in kcal mol<sup>-1</sup>.



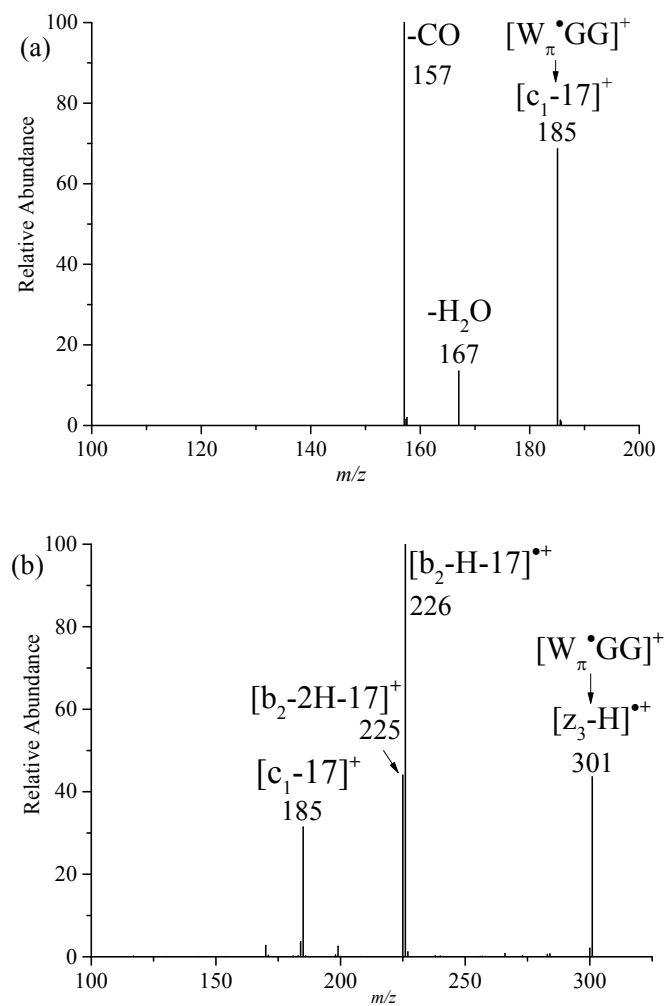
**Figure S1.** CID spectra of (a)  $[Y_{\pi} \bullet GGA]^+$  and (b)  $[z_4 - H]^{\bullet+}$  generated from  $[Y_{\pi} \bullet GGA]^+$ .



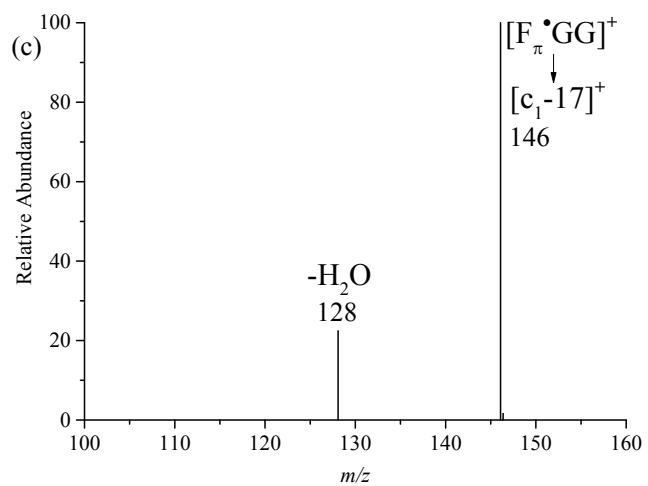
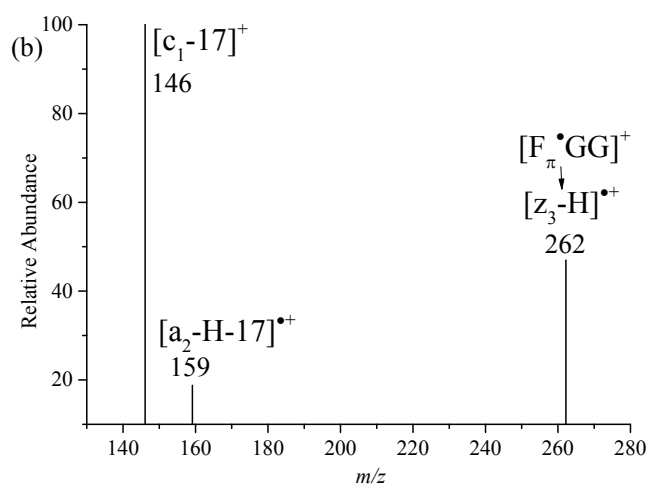
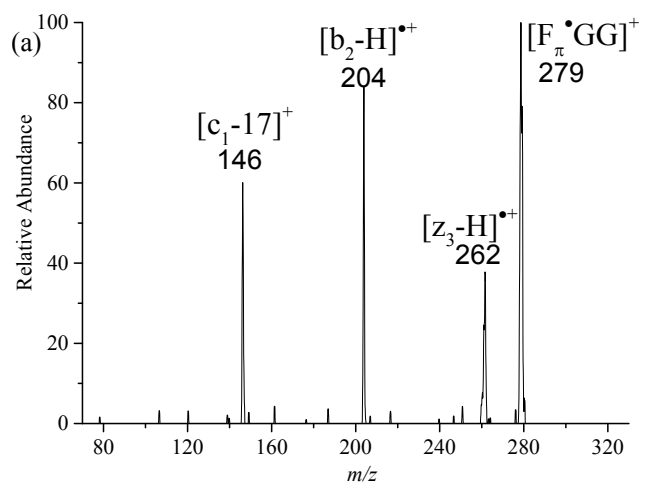
**Figure S2** CID spectra of (a)  $[Y_{\pi} \bullet GG]^+$  and (b)  $[z_3 - H]^{\bullet+}$  generated from  $[Y_{\pi} \bullet GG]^+$ .



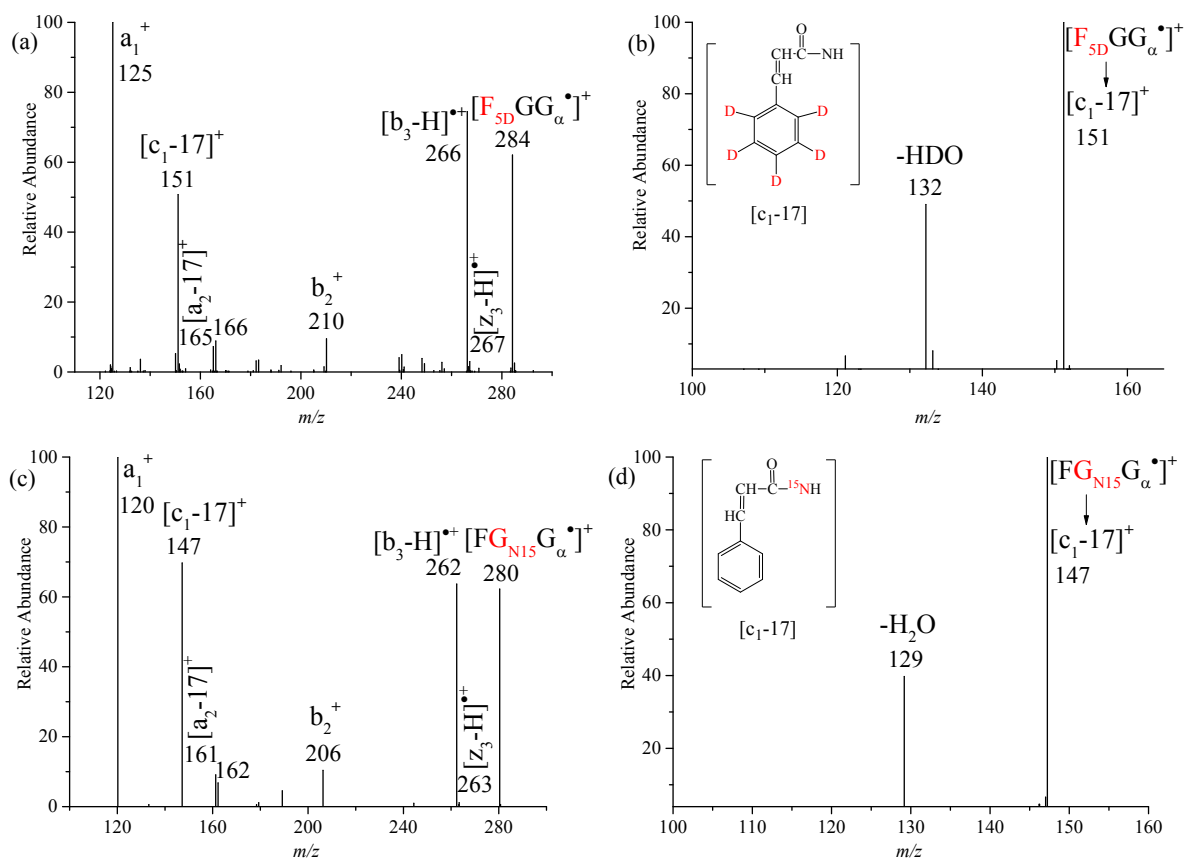
**Figure S3** CID spectra of (a)  $[c_1 - 17]^+$  and (b)  $[b_2 - H - 17]^+$  generated from  $[W_\pi \bullet GG]^+$ .



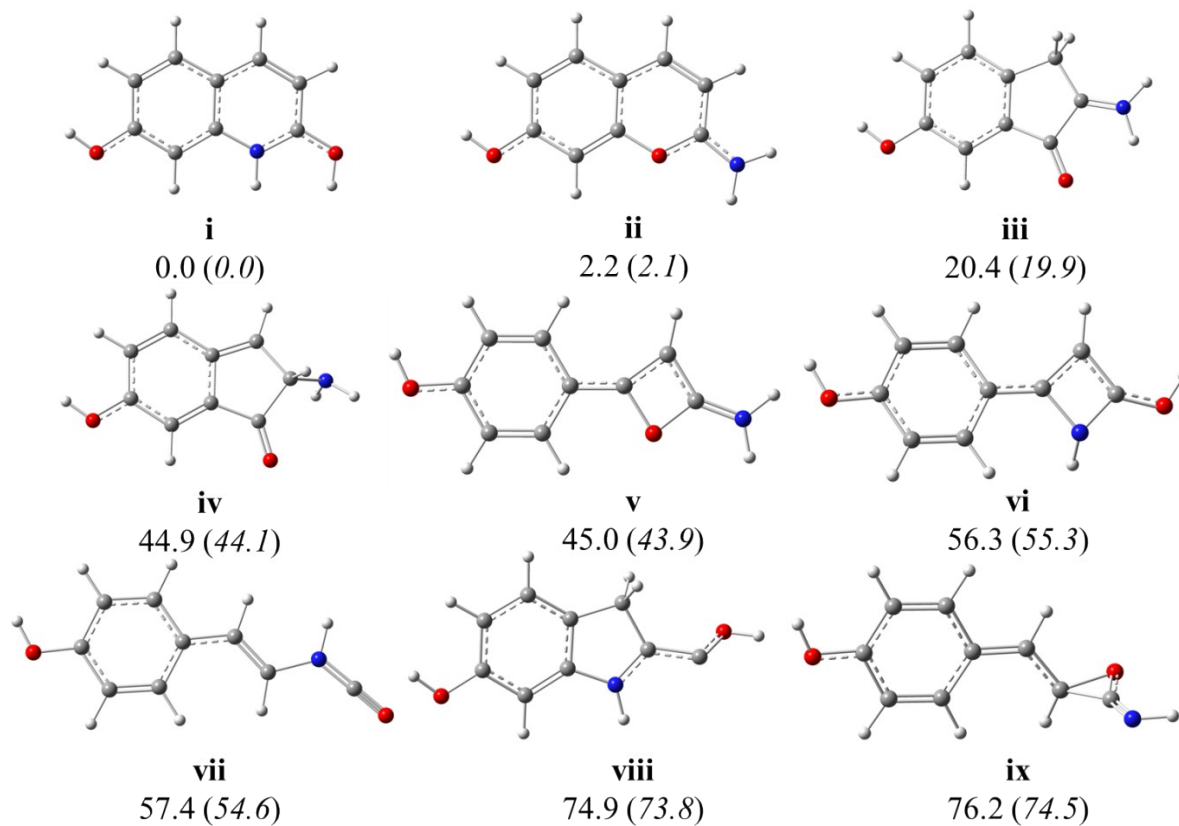
**Figure S4** CID spectra of (a)  $[F_{\pi} \bullet GG]^+$ , (b)  $[z_3-H]^+$  and (c)  $[c_1-17]^+$  generated from  $[F_{\pi} \bullet GG]^+$ .



**Figure S5.** CID spectra of (a)  $[F_{5D}GG_{\alpha}^{\bullet}]^+$ , (b)  $[c_1 - 17]^+$  generated from  $[F_{5D}GG_{\alpha}^{\bullet}]^+$ , (c)  $[FG_{N15}G_{\alpha}^{\bullet}]^+$  and (d)  $[c_1 - 17]^+$  generated from  $[FG_{N15}G_{\alpha}^{\bullet}]^+$ .

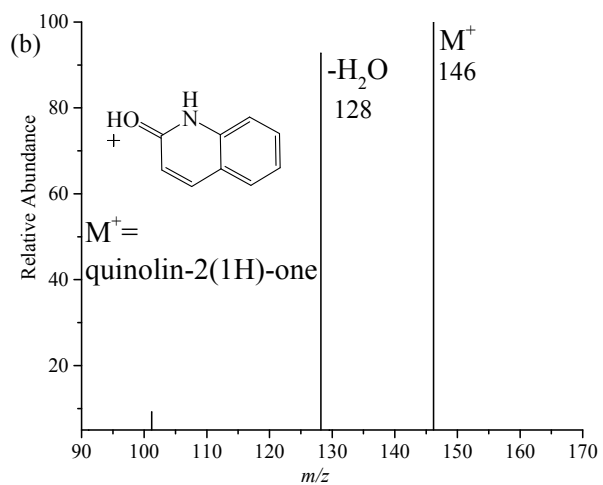
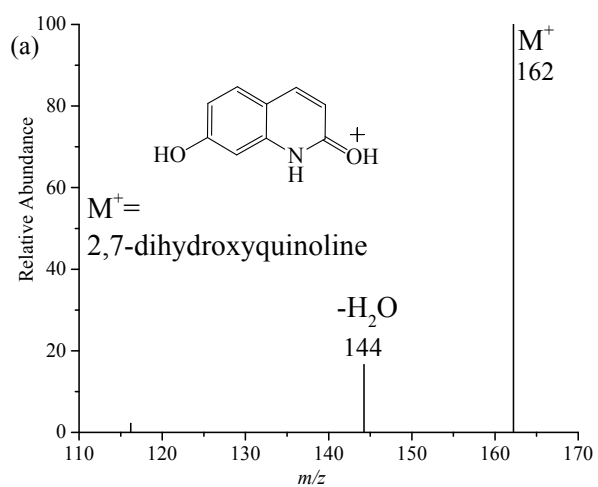


**Figure S6** Nine optimized structures proposed for  $[c_1-17]^+$ . The relative enthalpies ( $\Delta H^0$ ) and free energies ( $\Delta G^0_{298}$ , in parenthesis) are shown in kcal mol $^{-1}$ .

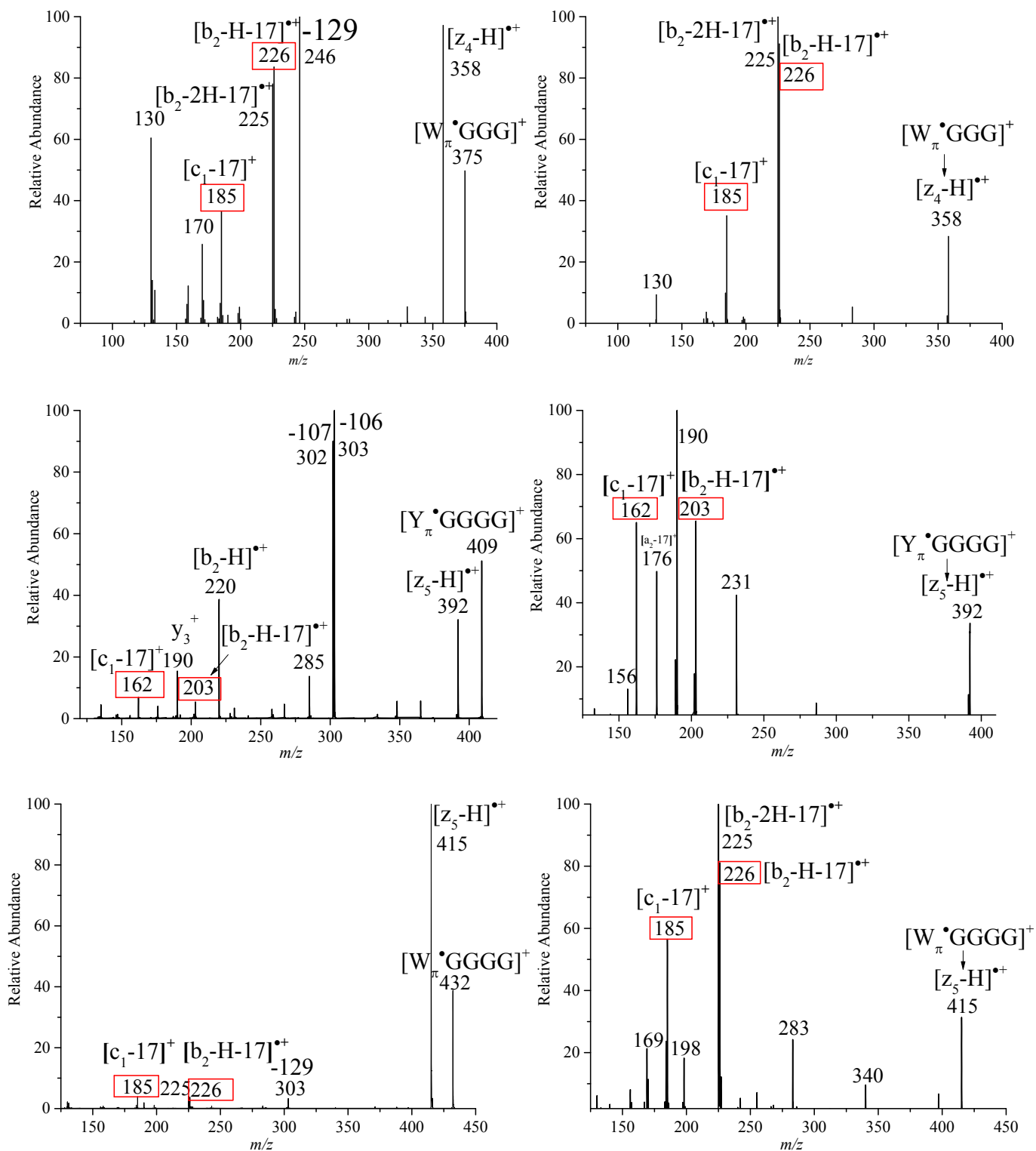


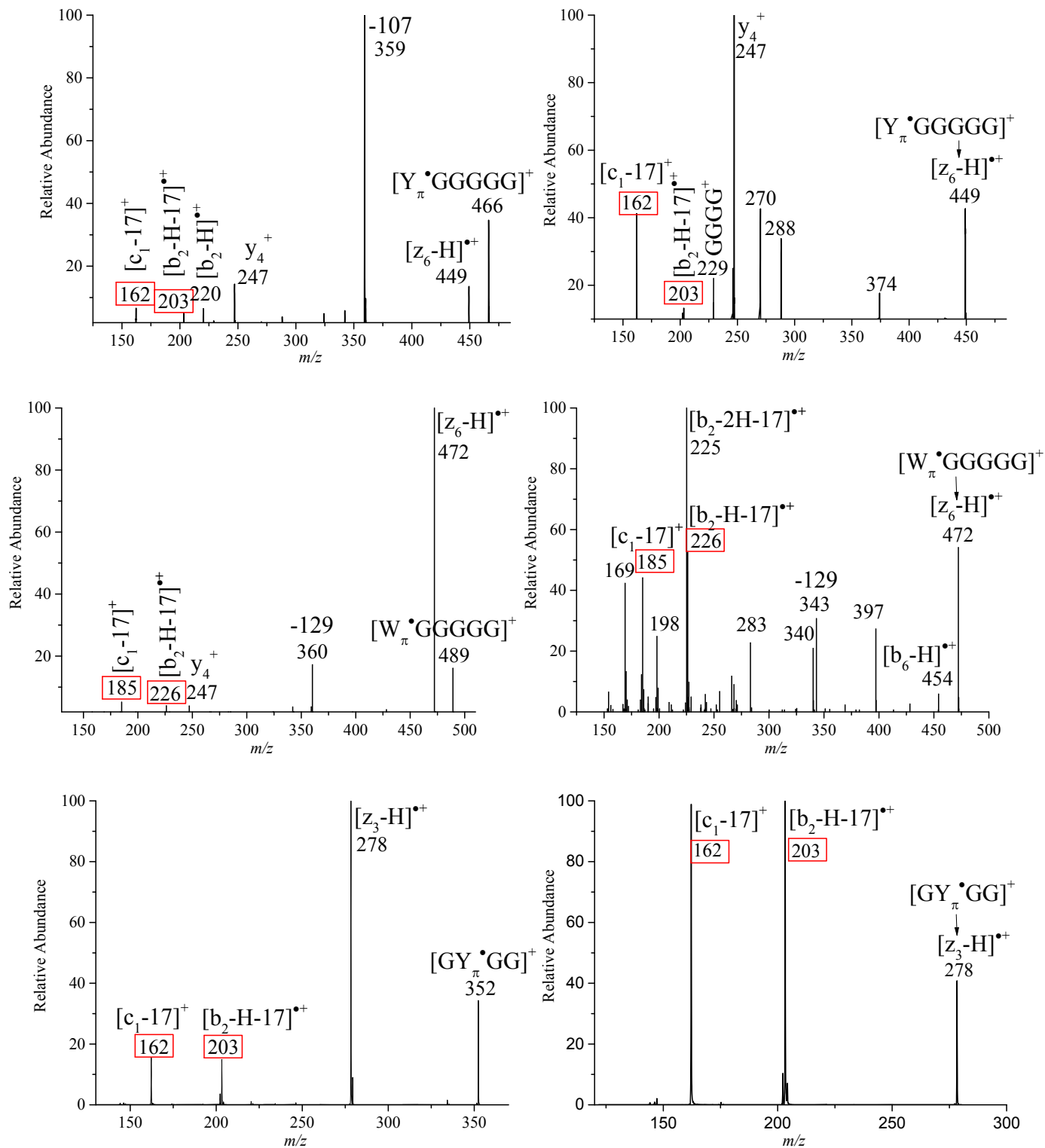


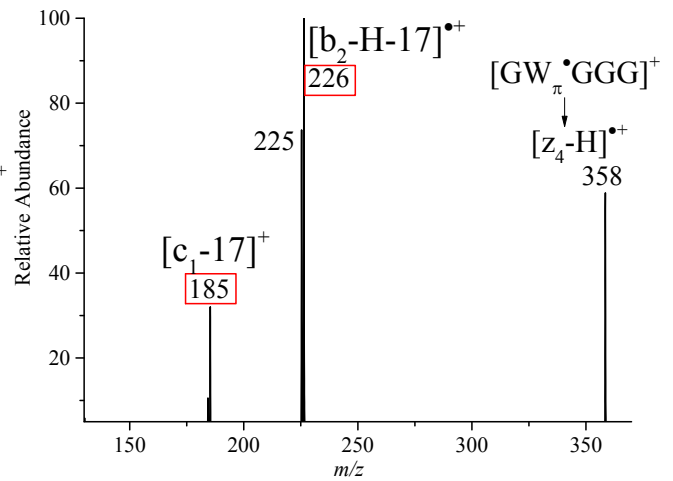
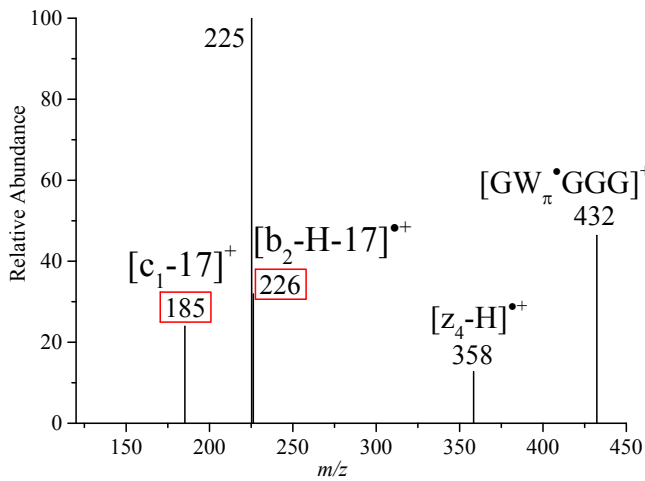
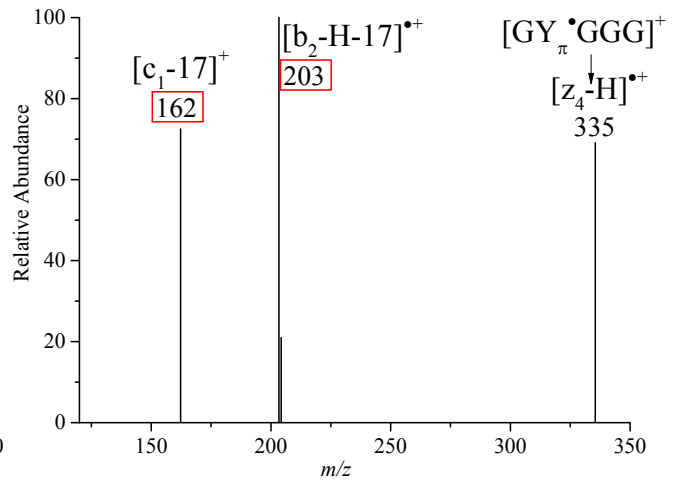
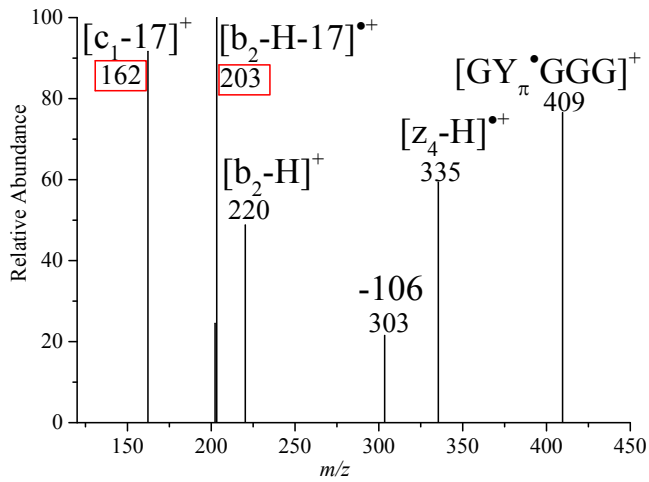
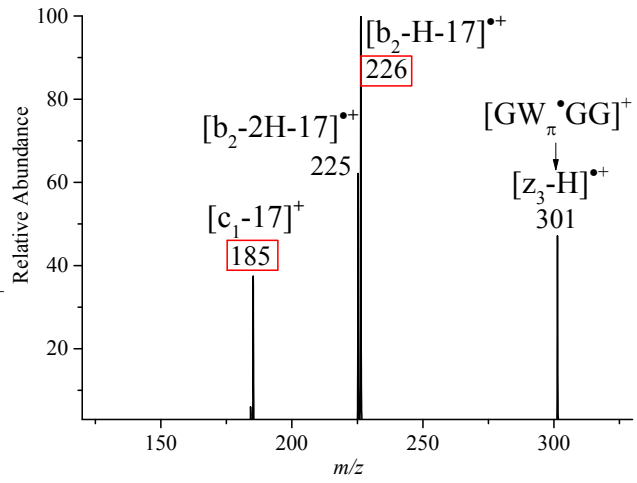
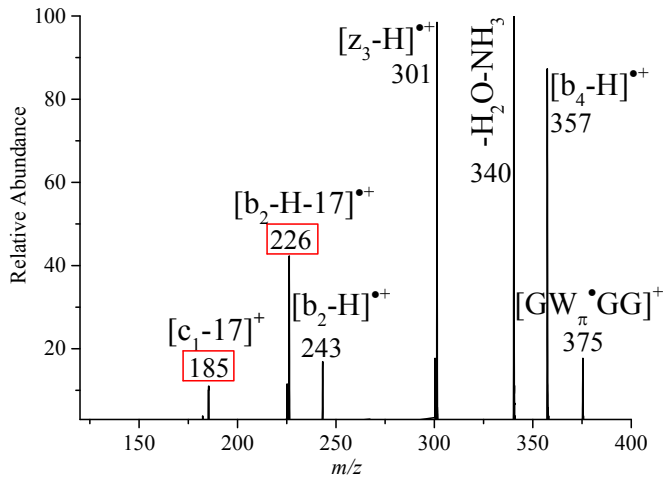
**Figure S7** CID spectra of (a) protonated 2,7-dihydroxyquinoline and (b) quinolin-2(1H)-one.

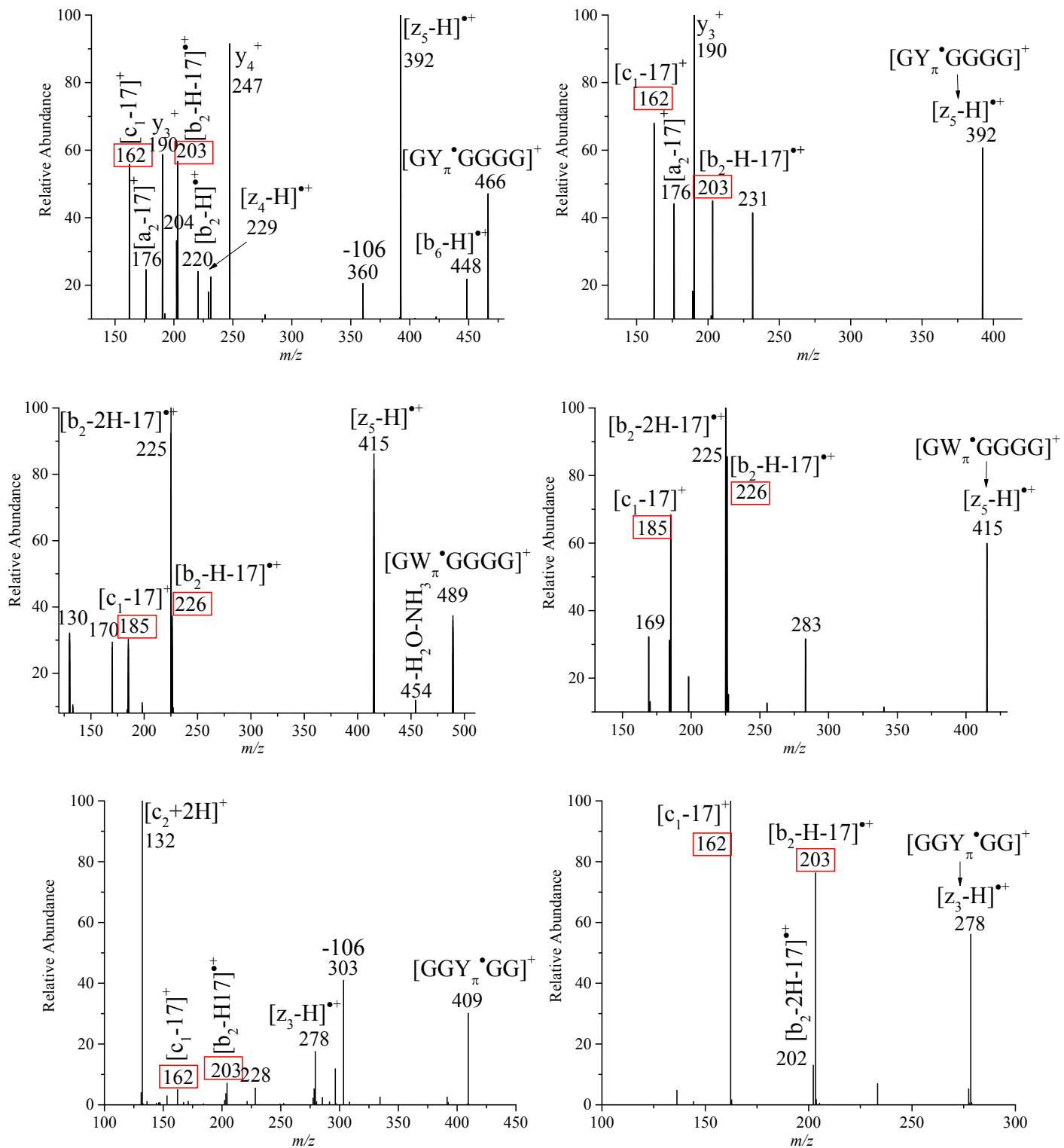


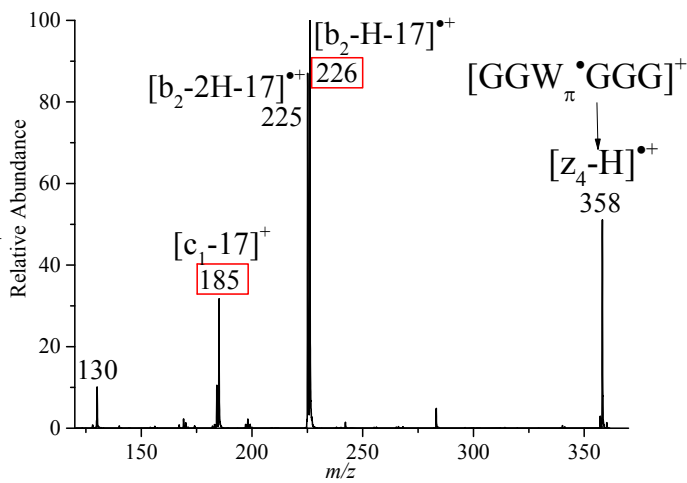
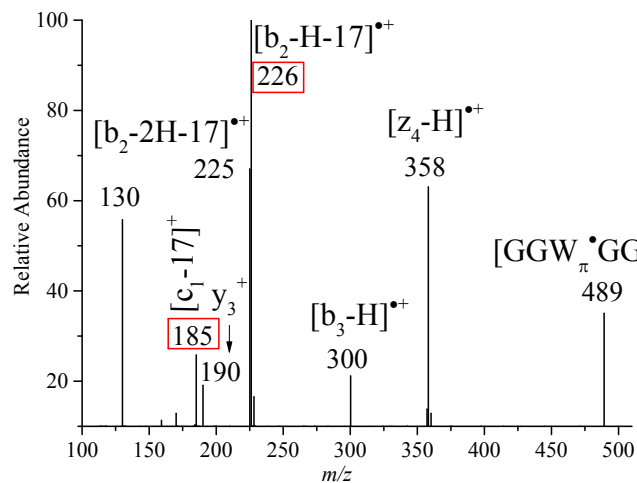
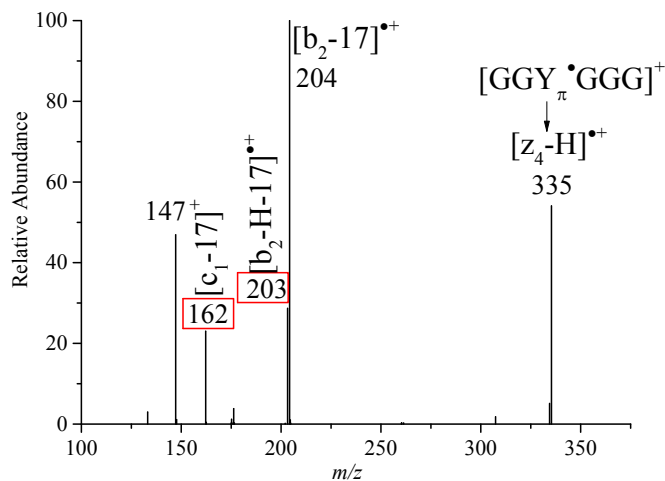
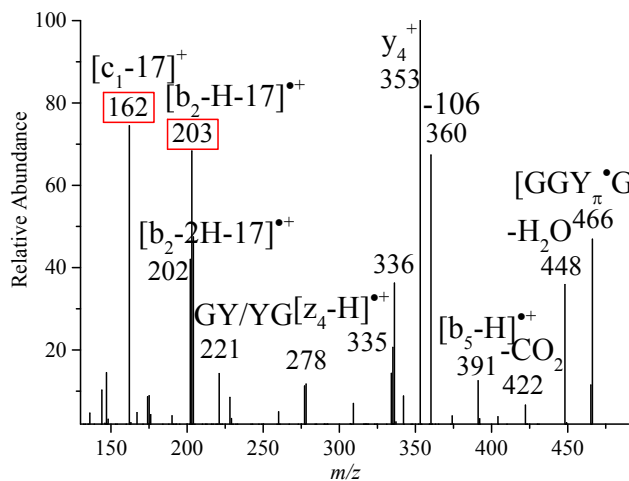
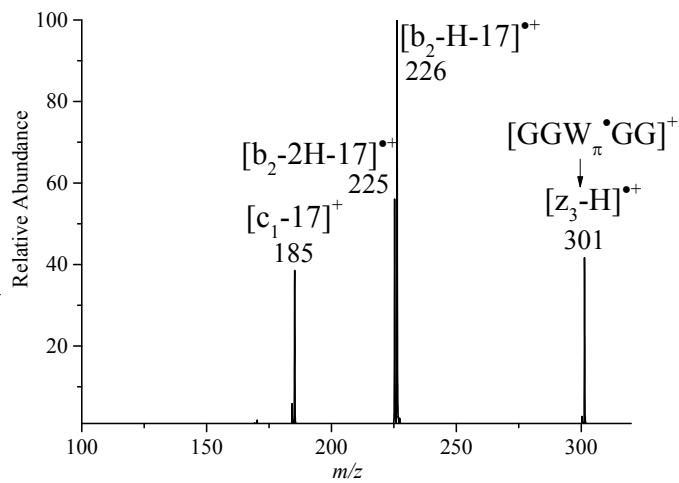
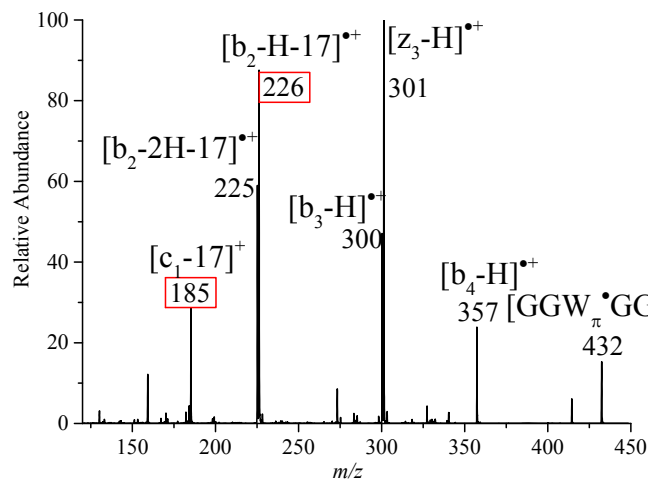
**Figure S8** CID spectra mentioned in Table 1.

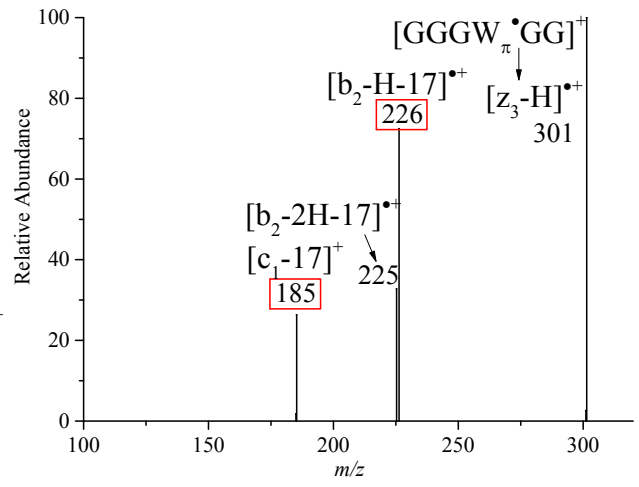
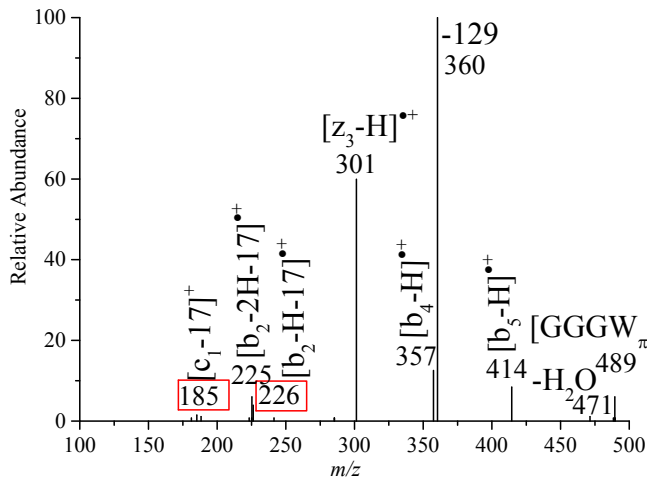
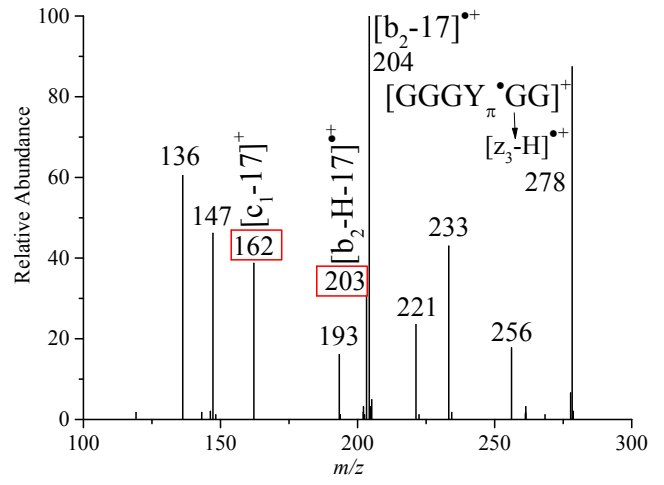
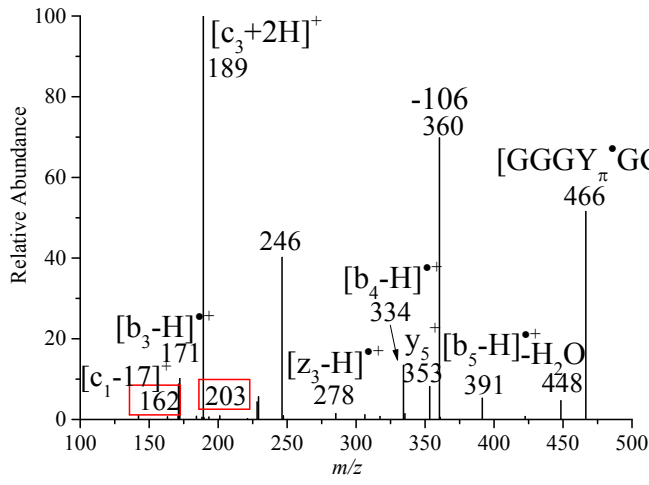




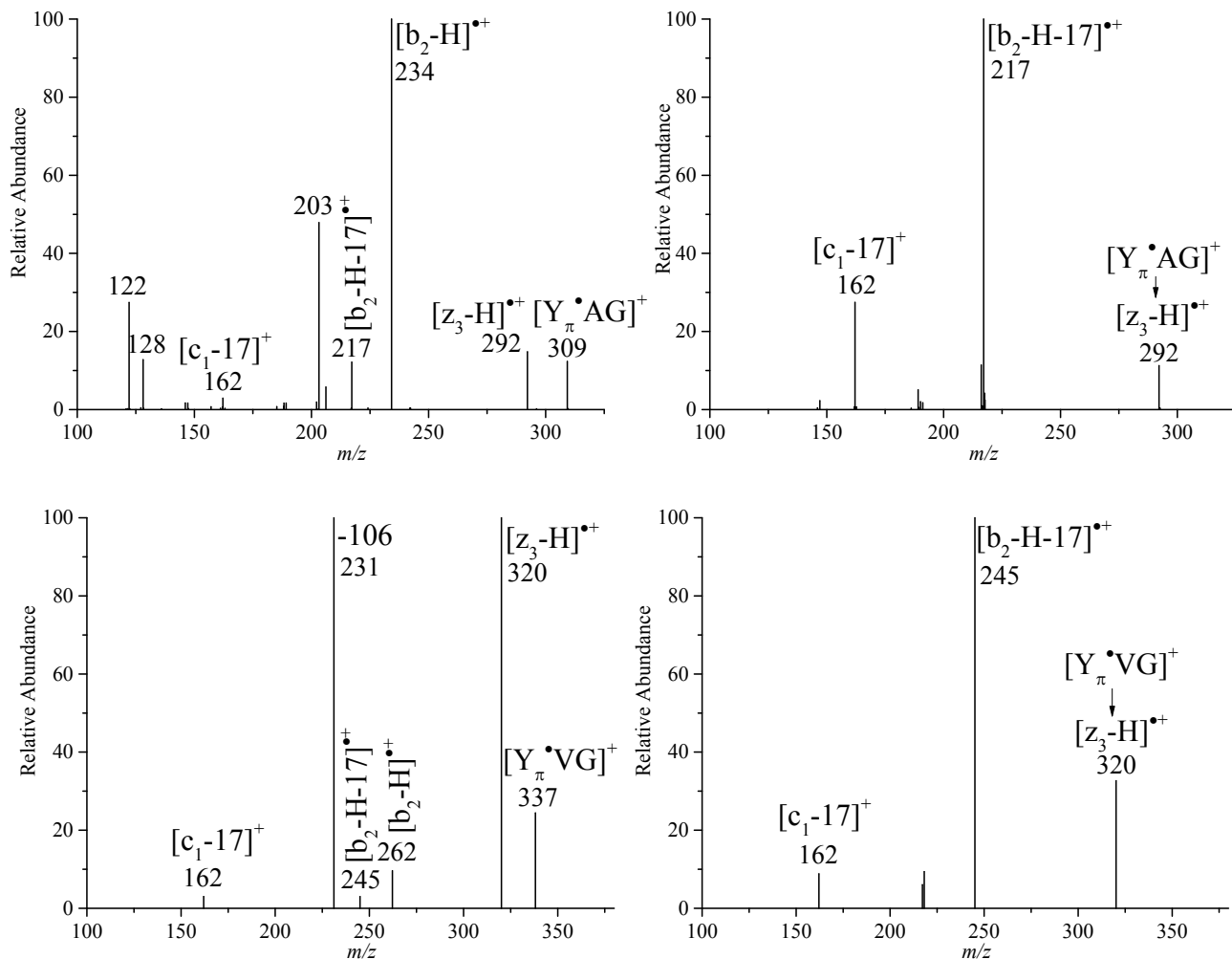




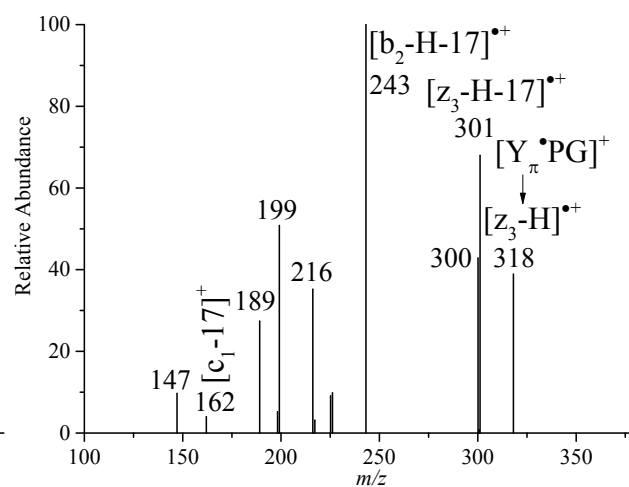
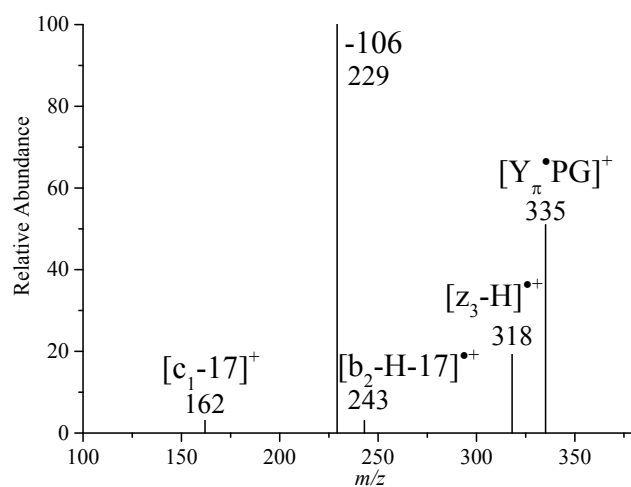
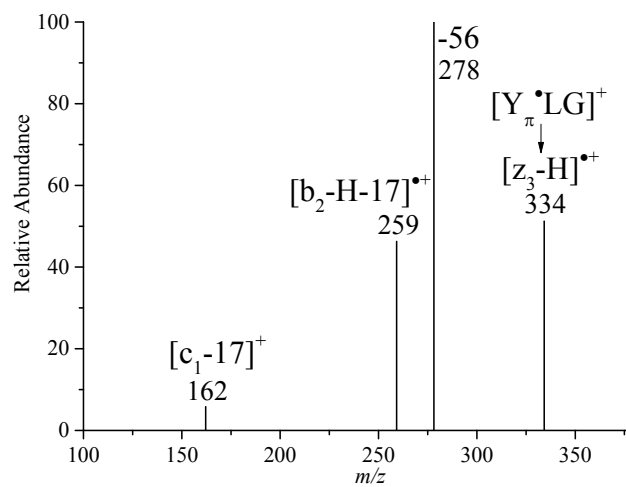
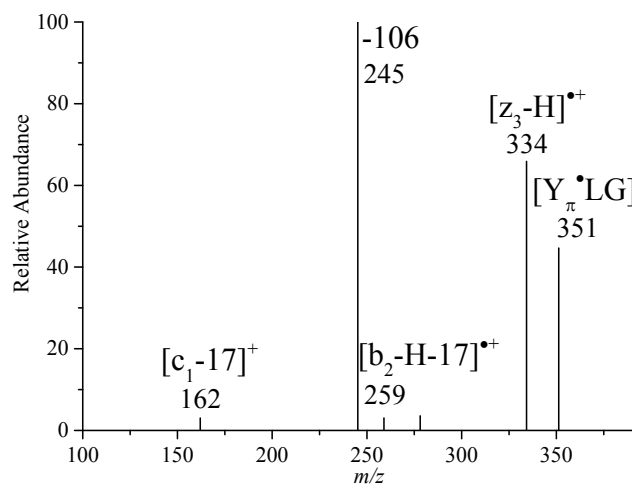




**Figure S9** CID spectra of  $[Y_{\pi} \cdot AG]^+$ ,  $[Y_{\pi} \cdot VG]^+$ ,  $[Y_{\pi} \cdot LG]^+$ ,  $[Y_{\pi} \cdot PG]^+$  and their  $[z_3-H]^{\bullet+}$ .







## Cartesian coordinate of selected structures optimized at the M06-2X/6-31++G(d,p) level

Structure\_1a.xyz

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|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.512709  | 0.169518  | 0.000028  |
| C | 0.233234  | 0.954660  | 0.000042  |
| O | 0.254281  | 2.177675  | 0.000032  |
| H | 1.470383  | -0.916413 | 0.000026  |
| C | 2.692705  | 0.870246  | 0.000015  |
| C | 3.997602  | 0.316945  | -0.000003 |
| H | 2.589488  | 1.954998  | 0.000016  |
| C | 6.628241  | -0.638740 | -0.000042 |
| C | 5.110273  | 1.220462  | -0.000025 |
| C | 4.264134  | -1.092688 | -0.000002 |
| C | 5.543711  | -1.562615 | -0.000022 |
| C | 6.398057  | 0.763235  | -0.000045 |
| H | 4.912372  | 2.288105  | -0.000027 |
| H | 3.441846  | -1.799329 | 0.000017  |
| H | 5.773850  | -2.622296 | -0.000020 |
| H | 7.238425  | 1.451158  | -0.000063 |
| N | -0.884803 | 0.210368  | 0.000063  |
| C | -2.191245 | 0.824240  | 0.000069  |
| C | -3.215117 | -0.309334 | 0.000078  |
| O | -2.852267 | -1.480356 | 0.000086  |
| H | -0.892704 | -0.807244 | 0.000068  |
| H | -2.315190 | 1.461172  | 0.883918  |
| H | -2.315198 | 1.461169  | -0.883781 |
| N | -4.503444 | 0.066602  | 0.000079  |
| C | -5.563448 | -0.915551 | 0.000057  |
| C | -6.885139 | -0.183011 | -0.000080 |
| O | -6.989602 | 1.019299  | -0.000158 |
| O | -7.913515 | -1.030629 | -0.000098 |
| H | -4.785513 | 1.041330  | 0.000038  |
| H | -5.507107 | -1.564052 | 0.881086  |
| H | -8.738592 | -0.518899 | -0.000183 |
| H | -5.506969 | -1.564149 | -0.880893 |
| O | 7.833175  | -1.162095 | -0.000057 |
| H | 8.541762  | -0.499685 | -0.000062 |

Structure\_1b.xyz

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.434128  | 1.558674  | 0.081338  |
| C | 0.513370  | 0.378559  | 0.125272  |
| O | 0.875454  | -0.792791 | 0.168774  |
| C | 2.806609  | 1.650973  | 0.018848  |
| C | 3.873659  | 0.704305  | -0.003154 |
| H | 3.154379  | 2.681082  | -0.031008 |
| C | 6.151067  | -0.931531 | -0.072047 |
| C | 3.752249  | -0.723083 | 0.101407  |
| C | 5.193336  | 1.265880  | -0.134665 |
| C | 6.307095  | 0.480314  | -0.172864 |
| C | 4.862524  | -1.516777 | 0.066855  |
| H | 2.762752  | -1.152635 | 0.205418  |
| H | 5.297983  | 2.344082  | -0.209349 |
| H | 7.297726  | 0.913023  | -0.277457 |
| H | 4.796606  | -2.596461 | 0.145013  |
| N | -0.781644 | 0.739552  | 0.109476  |
| C | -1.835221 | -0.246053 | 0.130818  |
| C | -3.156423 | 0.518558  | 0.048565  |
| O | -3.165380 | 1.742784  | -0.005710 |
| H | -1.108638 | 1.702984  | 0.065539  |
| H | -1.728907 | -0.937204 | -0.713624 |
| H | -1.786348 | -0.841048 | 1.050510  |
| N | -4.268579 | -0.232075 | 0.040987  |
| C | -5.575205 | 0.380069  | -0.044461 |
| C | -6.608910 | -0.721109 | -0.088792 |
| O | -6.341908 | -1.897614 | -0.048382 |
| O | -7.843790 | -0.228947 | -0.176090 |
| H | -4.242186 | -1.245698 | 0.077181  |
| H | -5.664078 | 1.002009  | -0.941720 |
| H | -8.472925 | -0.968016 | -0.198071 |
| H | -5.771411 | 1.027884  | 0.816959  |
| H | 0.924533  | 2.519871  | 0.085316  |
| O | 7.170052  | -1.758590 | -0.098474 |
| H | 8.026980  | -1.313626 | -0.191596 |

Structure\_2.xyz

|   |          |           |          |
|---|----------|-----------|----------|
| C | 3.359631 | -2.169245 | 0.238351 |
|---|----------|-----------|----------|

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.975230  | -2.384764 | -0.108452 |
| O | 1.409205  | -3.412919 | -0.329770 |
| C | 3.876697  | -0.920325 | 0.424517  |
| C | 3.148279  | 0.259633  | 0.116667  |
| H | 4.882997  | -0.816146 | 0.822340  |
| C | 1.506939  | 2.532238  | -0.324812 |
| C | 1.873671  | 0.099890  | -0.666305 |
| C | 3.587135  | 1.528500  | 0.484818  |
| C | 2.806541  | 2.653571  | 0.276405  |
| C | 1.032771  | 1.328748  | -0.741615 |
| H | 2.134516  | -0.236518 | -1.687372 |
| H | 4.547262  | 1.626540  | 0.983044  |
| H | 3.161759  | 3.629395  | 0.593117  |
| H | 0.070660  | 1.301418  | -1.241927 |
| N | 1.112180  | -1.091477 | -0.088317 |
| C | -0.239166 | -1.298676 | -0.668502 |
| C | -1.217109 | -0.633314 | 0.306937  |
| O | -0.809053 | -0.320874 | 1.422881  |
| H | 0.892664  | -0.853069 | 0.911868  |
| H | -0.282684 | -0.891399 | -1.680676 |
| H | -0.426270 | -2.374764 | -0.708163 |
| N | -2.465758 | -0.458416 | -0.121880 |
| C | -3.491630 | 0.089539  | 0.744441  |
| C | -4.794753 | 0.070761  | -0.025571 |
| O | -4.891880 | -0.343320 | -1.155057 |
| O | -5.794474 | 0.562167  | 0.697658  |
| H | -2.775772 | -0.760153 | -1.042055 |
| H | -3.252955 | 1.116206  | 1.040201  |
| H | -6.612777 | 0.527241  | 0.175258  |
| H | -3.593860 | -0.502232 | 1.659967  |
| H | 3.934957  | -3.072122 | 0.404524  |
| O | 0.724095  | 3.613783  | -0.499408 |
| H | 1.145985  | 4.424806  | -0.190445 |

Structure\_3.xyz

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|   |          |           |           |
|---|----------|-----------|-----------|
| C | 2.978076 | -2.353670 | 0.442016  |
| C | 1.822557 | -2.302317 | -0.276121 |
| O | 1.119306 | -3.282431 | -0.865882 |
| C | 3.566402 | -1.183485 | 0.947050  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 3.015799  | 0.087793  | 0.595361  |
| H | 4.476684  | -1.235023 | 1.530701  |
| C | 1.970147  | 2.547776  | -0.322317 |
| C | 1.827355  | 0.170762  | -0.151155 |
| C | 3.654355  | 1.311251  | 0.885107  |
| C | 3.145294  | 2.518103  | 0.443798  |
| C | 1.296578  | 1.357982  | -0.619573 |
| H | 0.624761  | -1.015102 | -1.342424 |
| H | 4.575720  | 1.293804  | 1.458873  |
| H | 3.661941  | 3.444087  | 0.679013  |
| H | 0.390630  | 1.393307  | -1.216396 |
| N | 1.044320  | -1.069234 | -0.382442 |
| C | -0.198605 | -1.128998 | 0.489657  |
| C | -1.344005 | -0.598941 | -0.380722 |
| O | -1.155032 | -0.476027 | -1.588798 |
| H | 1.604868  | -4.118838 | -0.877197 |
| H | -0.385025 | -2.175155 | 0.743914  |
| H | -0.017160 | -0.540565 | 1.390173  |
| N | -2.490588 | -0.329885 | 0.239049  |
| C | -3.660278 | 0.111872  | -0.496437 |
| C | -4.782379 | 0.297921  | 0.502445  |
| O | -4.657245 | 0.095144  | 1.685624  |
| O | -5.898025 | 0.706320  | -0.090737 |
| H | -2.609930 | -0.437121 | 1.243143  |
| H | -3.954645 | -0.624423 | -1.251374 |
| H | -6.595105 | 0.812555  | 0.577507  |
| H | -3.467798 | 1.056775  | -1.014814 |
| H | 3.453617  | -3.318850 | 0.584238  |
| O | 1.423958  | 3.680298  | -0.800299 |
| H | 1.953845  | 4.455672  | -0.575528 |

Structure\_4.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.284439 | 2.918139  | -0.157847 |
| C | -0.275001 | 2.081649  | 0.214031  |
| O | 1.069155  | 2.377194  | 0.258989  |
| C | -2.587876 | 2.415198  | -0.308015 |
| C | -2.811372 | 1.004413  | -0.209421 |
| H | -3.409445 | 3.075135  | -0.555337 |
| C | -3.164815 | -1.794008 | -0.068598 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.741191 | 0.141033  | 0.138690  |
| C | -4.057723 | 0.403249  | -0.464408 |
| C | -4.243084 | -0.969076 | -0.394740 |
| C | -1.909096 | -1.237156 | 0.197057  |
| H | 1.030835  | -0.325758 | -1.412944 |
| H | -4.896382 | 1.043000  | -0.721464 |
| H | -5.220348 | -1.400177 | -0.591675 |
| H | -1.107867 | -1.920410 | 0.462216  |
| N | -0.476287 | 0.714397  | 0.443464  |
| C | 0.405661  | 0.018214  | 1.354058  |
| C | 1.386810  | -0.851949 | 0.603192  |
| O | 1.855299  | -1.901065 | 0.871437  |
| H | 1.216063  | 3.327820  | 0.349592  |
| H | 1.005920  | 0.732525  | 1.930169  |
| H | -0.149589 | -0.619648 | 2.047113  |
| N | 1.805537  | -0.200561 | -0.749250 |
| C | 3.079787  | -0.760742 | -1.263442 |
| C | 4.163345  | -0.311851 | -0.296601 |
| O | 3.920394  | 0.416466  | 0.633938  |
| O | 5.340927  | -0.807423 | -0.625639 |
| H | 1.886406  | 0.820972  | -0.570133 |
| H | 3.270862  | -0.374332 | -2.266917 |
| H | 6.016936  | -0.509493 | 0.007310  |
| H | 3.015040  | -1.849916 | -1.293451 |
| H | -1.058591 | 3.958806  | -0.367579 |
| O | -3.250822 | -3.142006 | 0.014106  |
| H | -4.150245 | -3.443385 | -0.162778 |

Structure\_5a.xyz

20

|   |           |           |          |
|---|-----------|-----------|----------|
| C | -2.384225 | -1.094736 | 0.000000 |
| C | -2.397554 | 0.308472  | 0.000000 |
| O | -3.472170 | 1.076088  | 0.000000 |
| C | -1.163119 | -1.731151 | 0.000000 |
| C | 0.050909  | -1.010408 | 0.000000 |
| H | -1.128217 | -2.817257 | 0.000000 |
| C | 2.383270  | 0.545916  | 0.000000 |
| C | 0.000000  | 0.406508  | 0.000000 |
| C | 1.327452  | -1.628092 | 0.000000 |
| C | 2.468948  | -0.871935 | 0.000000 |

|   |           |           |          |
|---|-----------|-----------|----------|
| C | 1.152115  | 1.188648  | 0.000000 |
| H | -1.324007 | 2.010420  | 0.000000 |
| H | 1.388120  | -2.711915 | 0.000000 |
| H | 3.444640  | -1.348779 | 0.000000 |
| H | 1.116919  | 2.272860  | 0.000000 |
| N | -1.251478 | 0.995242  | 0.000000 |
| H | -4.296645 | 0.568916  | 0.000000 |
| H | -3.319441 | -1.641440 | 0.000000 |
| O | 3.467626  | 1.324696  | 0.000000 |
| H | 4.288558  | 0.814901  | 0.000000 |

Structure\_5b.xyz

20

|   |           |           |          |
|---|-----------|-----------|----------|
| C | -2.410885 | 1.012991  | 0.000000 |
| C | -2.347707 | -0.400706 | 0.000000 |
| C | -1.233606 | 1.709219  | 0.000000 |
| C | 0.017497  | 1.037250  | 0.000000 |
| H | -1.249805 | 2.795821  | 0.000000 |
| C | 2.379554  | -0.468631 | 0.000000 |
| C | 0.010037  | -0.369268 | 0.000000 |
| C | 1.274376  | 1.680103  | 0.000000 |
| C | 2.436245  | 0.944554  | 0.000000 |
| C | 1.154342  | -1.139062 | 0.000000 |
| H | -3.280369 | -2.205536 | 0.000000 |
| H | 1.313505  | 2.764996  | 0.000000 |
| H | 3.400689  | 1.443284  | 0.000000 |
| H | 1.116178  | -2.221787 | 0.000000 |
| H | -3.378291 | 1.498743  | 0.000000 |
| N | -3.401238 | -1.200730 | 0.000000 |
| H | -4.338002 | -0.823811 | 0.000000 |
| O | -1.192067 | -1.039133 | 0.000000 |
| O | 3.474344  | -1.232724 | 0.000000 |
| H | 4.287428  | -0.710436 | 0.000000 |

Structure\_6a.xyz

24

|   |          |           |           |
|---|----------|-----------|-----------|
| C | 2.707158 | 1.127464  | -0.110077 |
| C | 2.413808 | -0.243756 | -0.056636 |
| O | 3.261339 | -1.256575 | -0.199926 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.687072  | 2.059445  | -0.043046 |
| C | 0.337687  | 1.657427  | 0.128254  |
| H | 1.925795  | 3.114108  | -0.146153 |
| C | -2.266615 | 0.463251  | -0.025393 |
| C | 0.149284  | 0.295192  | 0.302064  |
| C | -0.848414 | 2.455787  | 0.003443  |
| C | -2.093080 | 1.828437  | -0.163034 |
| C | -1.154631 | -0.356347 | 0.562962  |
| H | -0.762301 | 3.531236  | -0.092043 |
| H | -2.961538 | 2.416550  | -0.441071 |
| H | -1.324123 | -0.451322 | 1.657722  |
| N | 1.140545  | -0.618840 | 0.145758  |
| C | 0.626701  | -2.004749 | 0.080998  |
| C | -0.897171 | -1.780042 | 0.071492  |
| O | -1.727328 | -2.578843 | -0.254801 |
| H | 4.165190  | -0.960338 | -0.378128 |
| H | 0.982214  | -2.503284 | -0.823217 |
| H | 0.933653  | -2.579197 | 0.960364  |
| H | 3.736840  | 1.438122  | -0.249174 |
| O | -3.441996 | -0.114908 | -0.267372 |
| H | -3.386464 | -1.084037 | -0.237971 |

Structure\_6b.xyz

24

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.655596  | 0.459278  | 0.538333  |
| C | 1.323863  | -0.930038 | 0.123440  |
| C | 0.603093  | 1.401519  | 0.057391  |
| C | -0.705958 | 0.898155  | -0.018428 |
| H | 0.840572  | 2.450828  | -0.066869 |
| C | -3.316584 | -0.216339 | -0.019474 |
| C | -0.961085 | -0.494571 | 0.073646  |
| C | -1.864246 | 1.710877  | -0.160265 |
| C | -3.132762 | 1.172699  | -0.155064 |
| C | -2.205265 | -1.067896 | 0.079113  |
| H | -1.731781 | 2.784224  | -0.251516 |
| H | -3.997031 | 1.823491  | -0.249545 |
| H | -2.339643 | -2.142044 | 0.135632  |
| H | 1.732622  | 0.467001  | 1.646645  |
| N | 2.374155  | -1.632620 | -0.208308 |
| H | 2.303581  | -2.586942 | -0.551071 |



|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 3.625023  | -0.855814 | -0.194721 |
| H | 4.281959  | -1.169398 | 0.622088  |
| H | 4.148760  | -0.944503 | -1.148531 |
| C | 3.105530  | 0.576050  | 0.035507  |
| O | 3.718349  | 1.582445  | -0.137154 |
| O | 0.129326  | -1.404517 | 0.039293  |
| O | -4.520507 | -0.804664 | 0.003460  |
| H | -5.238691 | -0.163946 | -0.080341 |

Structure\_7.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.784402 | -2.401450 | 0.126078  |
| C | -0.959792 | -1.227144 | 0.174628  |
| C | -3.131076 | -2.245357 | -0.062363 |
| C | -3.717719 | -0.958906 | 0.013608  |
| H | -3.748060 | -3.105389 | -0.308674 |
| C | -4.578373 | 1.743247  | -0.063581 |
| C | -2.873512 | 0.108381  | 0.636993  |
| C | -5.010278 | -0.652506 | -0.399891 |
| C | -5.452820 | 0.662312  | -0.427191 |
| C | -3.318667 | 1.501204  | 0.389184  |
| H | -2.856521 | -0.076225 | 1.729291  |
| H | -5.661720 | -1.448242 | -0.749242 |
| H | -6.457785 | 0.885897  | -0.773359 |
| H | -2.669838 | 2.320707  | 0.677445  |
| H | -1.297385 | -3.368067 | 0.089188  |
| N | 0.345103  | -1.284009 | 0.071968  |
| H | 0.832206  | -2.177686 | -0.042900 |
| C | 1.234905  | -0.136903 | 0.070435  |
| H | 1.010552  | 0.522444  | -0.774494 |
| H | 1.122288  | 0.435036  | 0.997184  |
| C | 2.651893  | -0.713193 | -0.052740 |
| O | 2.809773  | -1.923188 | -0.158942 |
| N | 3.648471  | 0.178069  | -0.037917 |
| H | 3.490525  | 1.176361  | 0.060325  |
| C | 5.029398  | -0.243153 | -0.146779 |
| C | 5.896647  | 0.992783  | -0.057029 |
| H | 5.296275  | -0.938886 | 0.655638  |
| H | 5.216537  | -0.754058 | -1.097271 |
| O | 5.456327  | 2.109159  | 0.075335  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| O | 7.188657  | 0.690105  | -0.141474 |
| H | 7.708392  | 1.507815  | -0.075492 |
| O | -1.470222 | -0.014482 | 0.235120  |
| O | -4.982356 | 3.024585  | -0.172903 |
| H | -5.875151 | 3.096550  | -0.531204 |

Structure\_8.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.872271 | -2.491412 | -0.228585 |
| C | -1.059818 | -1.484764 | 0.208538  |
| C | -3.208424 | -2.193013 | -0.506449 |
| C | -3.654199 | -0.842980 | -0.330285 |
| H | -3.893665 | -2.959333 | -0.844988 |
| C | -4.409943 | 1.845213  | 0.057906  |
| C | -2.746345 | 0.140265  | 0.118602  |
| C | -4.970507 | -0.412511 | -0.578652 |
| C | -5.349186 | 0.904810  | -0.391576 |
| C | -3.091063 | 1.459957  | 0.316811  |
| H | 0.597668  | -1.254646 | 1.462714  |
| H | -5.699000 | -1.138485 | -0.926344 |
| H | -6.371586 | 1.212038  | -0.590847 |
| H | -2.368130 | 2.185304  | 0.671212  |
| H | -1.476590 | -3.495221 | -0.345673 |
| N | 0.353143  | -1.616938 | 0.511902  |
| H | 0.599489  | -2.611206 | 0.528038  |
| C | 1.284804  | -0.865781 | -0.402376 |
| H | 1.531918  | -1.490794 | -1.261525 |
| H | 0.755721  | 0.031177  | -0.732525 |
| C | 2.491917  | -0.486525 | 0.465142  |
| O | 2.386426  | -0.596297 | 1.683598  |
| N | 3.571166  | -0.038602 | -0.171903 |
| H | 3.624416  | 0.027339  | -1.185281 |
| C | 4.749588  | 0.400240  | 0.551866  |
| C | 5.782414  | 0.812470  | -0.475615 |
| H | 4.520803  | 1.247513  | 1.206537  |
| H | 5.149562  | -0.403057 | 1.178875  |
| O | 5.587207  | 0.764098  | -1.665866 |
| O | 6.904792  | 1.225381  | 0.100188  |
| H | 7.541284  | 1.480926  | -0.587927 |
| O | -1.424123 | -0.195724 | 0.387178  |

|   |           |          |          |
|---|-----------|----------|----------|
| O | -4.707935 | 3.141874 | 0.263476 |
| H | -5.634778 | 3.326771 | 0.067183 |

TS\_la-1b.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.517006  | -1.381685 | -0.391418 |
| C | 0.484769  | -0.583097 | 0.306593  |
| O | 0.803616  | 0.100829  | 1.278430  |
| H | 1.320795  | -1.966068 | -1.286777 |
| C | 2.798492  | -1.503226 | 0.298739  |
| C | 3.891446  | -0.702348 | 0.101972  |
| H | 2.875929  | -2.285210 | 1.060741  |
| C | 6.127081  | 0.930972  | -0.214301 |
| C | 5.085544  | -0.933601 | 0.873450  |
| C | 3.870717  | 0.396592  | -0.831777 |
| C | 4.961904  | 1.194313  | -0.987884 |
| C | 6.182661  | -0.139896 | 0.719803  |
| H | 5.099665  | -1.755287 | 1.584110  |
| H | 2.964231  | 0.585675  | -1.399248 |
| H | 4.981229  | 2.033690  | -1.673525 |
| H | 7.087042  | -0.308183 | 1.296601  |
| N | -0.762081 | -0.659926 | -0.192326 |
| C | -1.860683 | 0.044311  | 0.425171  |
| C | -3.127549 | -0.359071 | -0.328051 |
| O | -3.075185 | -1.133865 | -1.275783 |
| H | -1.020320 | -1.256793 | -0.974225 |
| H | -1.939771 | -0.220433 | 1.485998  |
| H | -1.709335 | 1.128615  | 0.367396  |
| N | -4.271116 | 0.186915  | 0.117068  |
| C | -5.532892 | -0.119217 | -0.516896 |
| C | -6.619216 | 0.653502  | 0.194116  |
| O | -6.420579 | 1.394496  | 1.125933  |
| O | -7.818047 | 0.413659  | -0.336873 |
| H | -4.298481 | 0.827830  | 0.902803  |
| H | -5.756124 | -1.190620 | -0.466659 |
| H | -8.481304 | 0.928707  | 0.150064  |
| H | -5.523995 | 0.157041  | -1.576870 |
| O | 7.140689  | 1.738725  | -0.413829 |
| H | 7.913194  | 1.536072  | 0.136286  |

TS\_1b-2.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -3.837071 | -1.410837 | -0.304575 |
| C | -2.549194 | -2.051243 | 0.038749  |
| O | -2.398911 | -3.168646 | 0.449057  |
| C | -3.986843 | -0.068440 | -0.361094 |
| C | -2.922739 | 0.848859  | 0.007724  |
| H | -4.924745 | 0.350094  | -0.718734 |
| C | -0.582335 | 2.344565  | 0.509102  |
| C | -1.901653 | 0.367794  | 0.942410  |
| C | -2.739133 | 2.077732  | -0.620380 |
| C | -1.578450 | 2.808985  | -0.406718 |
| C | -0.765438 | 1.177303  | 1.215510  |
| H | -2.254699 | -0.261651 | 1.759999  |
| H | -3.481464 | 2.439614  | -1.324994 |
| H | -1.419605 | 3.743194  | -0.937670 |
| H | -0.060074 | 0.909465  | 1.994547  |
| N | -1.400475 | -1.170901 | -0.119488 |
| C | -0.085994 | -1.691975 | 0.242538  |
| C | 0.924392  | -0.809594 | -0.497074 |
| O | 0.543792  | -0.117543 | -1.438057 |
| H | -1.321088 | -0.720662 | -1.045519 |
| H | 0.044891  | -1.666493 | 1.328768  |
| H | -0.003584 | -2.735145 | -0.083672 |
| N | 2.187097  | -0.858167 | -0.065286 |
| C | 3.231108  | -0.096800 | -0.719226 |
| C | 4.523125  | -0.348112 | 0.026866  |
| O | 4.605396  | -1.068590 | 0.991255  |
| O | 5.536089  | 0.321565  | -0.514870 |
| H | 2.476251  | -1.438286 | 0.717171  |
| H | 3.002219  | 0.974083  | -0.705384 |
| H | 6.346628  | 0.130158  | -0.014949 |
| H | 3.346232  | -0.394701 | -1.766790 |
| H | -4.650604 | -2.092897 | -0.525674 |
| O | 0.524678  | 3.054786  | 0.748229  |
| H | 0.526291  | 3.904712  | 0.288430  |

TS\_1b-7.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.732957 | -2.318755 | 0.177462  |
| C | -0.914165 | -1.089291 | 0.226697  |
| C | -3.067642 | -2.243872 | 0.007753  |
| C | -3.766968 | -0.973577 | 0.040788  |
| H | -3.631491 | -3.144779 | -0.224320 |
| C | -4.753543 | 1.653424  | -0.074366 |
| C | -3.258755 | 0.059597  | 0.930294  |
| C | -4.816035 | -0.677593 | -0.830012 |
| C | -5.295040 | 0.618211  | -0.910620 |
| C | -3.770199 | 1.374474  | 0.846051  |
| H | -2.872109 | -0.266994 | 1.891906  |
| H | -5.212577 | -1.446369 | -1.485491 |
| H | -6.080533 | 0.865351  | -1.619727 |
| H | -3.441487 | 2.145131  | 1.532603  |
| H | -1.213276 | -3.270958 | 0.161199  |
| N | 0.395565  | -1.218432 | 0.127862  |
| H | 0.852217  | -2.127450 | 0.030650  |
| C | 1.307438  | -0.092238 | 0.110888  |
| H | 1.079384  | 0.570767  | -0.730709 |
| H | 1.215011  | 0.487189  | 1.035545  |
| C | 2.713995  | -0.682961 | -0.026552 |
| O | 2.865247  | -1.895302 | -0.115710 |
| N | 3.719514  | 0.201169  | -0.041149 |
| H | 3.568724  | 1.201597  | 0.041882  |
| C | 5.094387  | -0.233121 | -0.161200 |
| C | 5.974890  | 0.995418  | -0.114519 |
| H | 5.369522  | -0.911978 | 0.652970  |
| H | 5.263458  | -0.768234 | -1.101789 |
| O | 5.550407  | 2.119853  | -0.000648 |
| O | 7.263166  | 0.677576  | -0.213625 |
| H | 7.790417  | 1.492117  | -0.175460 |
| O | -1.425018 | 0.069489  | 0.309121  |
| O | -5.230069 | 2.899382  | -0.130773 |
| H | -5.975119 | 2.989180  | -0.739152 |

TS\_2-3.xyz

34

|   |           |          |           |
|---|-----------|----------|-----------|
| C | 1.773805  | 2.770022 | 0.605306  |
| C | 0.895532  | 2.337496 | -0.359617 |
| O | -0.002370 | 3.126050 | -0.965442 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 2.665995  | 1.852213  | 1.200121  |
| C | 2.678783  | 0.529933  | 0.794684  |
| H | 3.367412  | 2.192675  | 1.954396  |
| C | 2.972687  | -2.007819 | -0.440842 |
| C | 1.688654  | 0.040292  | -0.153620 |
| C | 3.642135  | -0.414922 | 1.270161  |
| C | 3.777918  | -1.639207 | 0.690009  |
| C | 1.999523  | -1.168159 | -0.899740 |
| H | 0.675301  | -0.425381 | 0.599745  |
| H | 4.307986  | -0.112675 | 2.072681  |
| H | 4.530235  | -2.334041 | 1.053845  |
| H | 1.407729  | -1.483080 | -1.751304 |
| N | 0.860836  | 1.045657  | -0.815253 |
| C | -0.402687 | 0.537433  | -1.335408 |
| C | -1.202173 | -0.100988 | -0.196946 |
| O | -0.609497 | -0.568520 | 0.809760  |
| H | 0.072371  | 4.038216  | -0.654546 |
| H | -0.965454 | 1.347594  | -1.796368 |
| H | -0.217344 | -0.218189 | -2.103236 |
| N | -2.513894 | -0.161121 | -0.303381 |
| C | -3.351791 | -0.791940 | 0.703086  |
| C | -4.791326 | -0.605644 | 0.267764  |
| O | -5.102548 | -0.027414 | -0.744264 |
| O | -5.633396 | -1.151816 | 1.134368  |
| H | -3.006991 | 0.251960  | -1.093380 |
| H | -3.196186 | -0.332192 | 1.683810  |
| H | -6.545111 | -1.014563 | 0.827131  |
| H | -3.123195 | -1.858503 | 0.793780  |
| H | 1.784745  | 3.819074  | 0.876868  |
| O | 3.156885  | -3.182971 | -1.079762 |
| H | 3.924985  | -3.657535 | -0.740012 |

TS\_3-4.xyz

34

|   |           |          |           |
|---|-----------|----------|-----------|
| C | -1.477717 | 2.890078 | -0.456308 |
| C | -0.393528 | 2.246815 | 0.055392  |
| O | 0.847016  | 2.736551 | 0.304030  |
| C | -2.667377 | 2.190307 | -0.714752 |
| C | -2.706489 | 0.775807 | -0.509609 |
| H | -3.536558 | 2.705627 | -1.102944 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -2.685773 | -2.029449 | -0.159334 |
| C | -1.587149 | 0.099337  | 0.011389  |
| C | -3.827518 | -0.017126 | -0.833842 |
| C | -3.826095 | -1.388662 | -0.664454 |
| C | -1.560274 | -1.276529 | 0.182221  |
| H | 0.679573  | 0.323110  | -0.119675 |
| H | -4.711358 | 0.472909  | -1.230664 |
| H | -4.705475 | -1.970788 | -0.924062 |
| H | -0.699468 | -1.802163 | 0.588596  |
| N | -0.393074 | 0.848665  | 0.393946  |
| C | 0.090578  | 0.574481  | 1.797026  |
| C | 1.365255  | -0.249367 | 1.641901  |
| O | 1.837939  | -0.991029 | 2.444395  |
| H | 0.913941  | 3.673830  | 0.076706  |
| H | 0.316059  | 1.515993  | 2.303839  |
| H | -0.652217 | 0.012398  | 2.364921  |
| N | 1.864845  | -0.081632 | 0.279301  |
| C | 2.700706  | -1.170341 | -0.248536 |
| C | 3.870453  | -0.538208 | -0.978875 |
| O | 4.074523  | 0.651776  | -0.969039 |
| O | 4.610531  | -1.446317 | -1.593635 |
| H | 2.394328  | 0.806512  | 0.189291  |
| H | 2.127600  | -1.805857 | -0.927303 |
| H | 5.364258  | -1.014423 | -2.029932 |
| H | 3.080427  | -1.784091 | 0.575877  |
| H | -1.396632 | 3.948517  | -0.682823 |
| O | -2.598954 | -3.361647 | 0.026830  |
| H | -3.415756 | -3.808345 | -0.228500 |

TS\_3-5a.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -2.127850 | 2.811500  | 0.041800  |
| C | -1.008038 | 2.147810  | -0.439307 |
| O | 0.139062  | 2.697385  | -0.850800 |
| C | -3.229962 | 2.078226  | 0.447841  |
| C | -3.230052 | 0.663094  | 0.326645  |
| H | -4.113837 | 2.583964  | 0.821731  |
| C | -3.154429 | -2.119973 | -0.088192 |
| C | -2.076631 | 0.012235  | -0.158146 |
| C | -4.357102 | -0.144172 | 0.610839  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -4.324470 | -1.504087 | 0.411438  |
| C | -2.021373 | -1.361732 | -0.366034 |
| H | -0.231269 | 0.339400  | -1.093459 |
| H | -5.259894 | 0.327803  | 0.986316  |
| H | -5.198463 | -2.109737 | 0.632836  |
| H | -1.127299 | -1.845081 | -0.750049 |
| N | -0.896204 | 0.773166  | -0.379552 |
| C | 0.456696  | 0.316229  | 0.915390  |
| C | 1.527109  | -0.117409 | -0.050019 |
| O | 1.200734  | -0.428054 | -1.206527 |
| H | 0.080566  | 3.661403  | -0.901114 |
| H | 0.635937  | 1.214498  | 1.502820  |
| H | -0.058194 | -0.487542 | 1.435749  |
| N | 2.786142  | -0.144679 | 0.380513  |
| C | 3.872097  | -0.564548 | -0.483743 |
| C | 5.157833  | -0.452001 | 0.306250  |
| O | 5.203777  | -0.079412 | 1.453125  |
| O | 6.208653  | -0.814304 | -0.422122 |
| H | 3.036637  | 0.103773  | 1.333534  |
| H | 3.927716  | 0.065501  | -1.377268 |
| H | 7.012393  | -0.730099 | 0.116797  |
| H | 3.735657  | -1.597811 | -0.819729 |
| H | -2.130234 | 3.895734  | 0.066067  |
| O | -3.070014 | -3.440480 | -0.310611 |
| H | -3.899944 | -3.893339 | -0.114057 |

TS\_4-6a.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 0.094498  | 3.065602  | -0.237748 |
| C | 0.645117  | 2.210663  | 0.698194  |
| O | 1.767284  | 2.393684  | 1.401495  |
| C | -1.046809 | 2.679758  | -0.939919 |
| C | -1.698268 | 1.452927  | -0.664210 |
| H | -1.445669 | 3.331654  | -1.710062 |
| C | -2.782490 | -1.090723 | 0.001330  |
| C | -1.192162 | 0.690074  | 0.418820  |
| C | -2.776790 | 0.895294  | -1.395956 |
| C | -3.271285 | -0.378818 | -1.082183 |
| C | -1.716033 | -0.570939 | 0.814206  |
| H | -0.214118 | -1.875990 | -1.041624 |



|   |           |           |           |
|---|-----------|-----------|-----------|
| H | -3.197309 | 1.451145  | -2.226302 |
| H | -4.084317 | -0.793904 | -1.671931 |
| H | -1.745280 | -0.854750 | 1.864692  |
| N | 0.013170  | 1.031049  | 0.978574  |
| C | 0.643971  | -0.059949 | 1.694497  |
| C | 0.249059  | -1.369415 | 0.960377  |
| O | 0.412039  | -2.467806 | 1.418745  |
| H | 2.248289  | 3.172222  | 1.091838  |
| H | 1.723521  | 0.092835  | 1.737078  |
| H | 0.251181  | -0.178726 | 2.708772  |
| N | 0.550987  | -1.322732 | -0.644713 |
| C | 1.863146  | -1.916109 | -0.987731 |
| C | 2.904417  | -0.819599 | -0.899464 |
| O | 2.617570  | 0.334311  | -0.673983 |
| O | 4.121370  | -1.286182 | -1.113055 |
| H | 0.493045  | -0.366530 | -1.015191 |
| H | 1.850025  | -2.325986 | -2.001029 |
| H | 4.768441  | -0.561796 | -1.073050 |
| H | 2.073337  | -2.726579 | -0.283083 |
| H | 0.575112  | 4.017532  | -0.432827 |
| O | -3.255593 | -2.289859 | 0.407069  |
| H | -4.044950 | -2.545114 | -0.087744 |

TS\_7-6b.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 2.259979  | -1.916313 | 0.854434  |
| C | 2.231819  | -1.216300 | -0.327590 |
| C | 1.051555  | -2.425184 | 1.375815  |
| C | -0.152403 | -2.030608 | 0.794433  |
| H | 1.051767  | -3.032808 | 2.274214  |
| C | -2.494282 | -1.314219 | -0.649603 |
| C | -0.103401 | -1.179212 | -0.374554 |
| C | -1.444802 | -2.360934 | 1.289721  |
| C | -2.573361 | -2.001147 | 0.603300  |
| C | -1.271469 | -0.975035 | -1.174952 |
| H | 0.094124  | 0.179223  | 0.027616  |
| H | -1.523528 | -2.937021 | 2.206688  |
| H | -3.551097 | -2.270847 | 0.994488  |
| H | -1.200771 | -0.484255 | -2.140436 |
| H | 3.191067  | -1.994242 | 1.403238  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| N | 3.225783  | -0.451828 | -0.871230 |
| H | 4.096452  | -0.480572 | -0.352923 |
| C | 2.793397  | 0.906169  | -1.246075 |
| H | 3.682645  | 1.510934  | -1.424617 |
| H | 2.193736  | 0.865736  | -2.156352 |
| C | 2.031476  | 1.516706  | -0.063786 |
| O | 2.567142  | 1.896369  | 0.941342  |
| N | 0.587323  | 1.447658  | -0.121695 |
| H | 0.209957  | 1.646658  | -1.058049 |
| C | -0.130496 | 2.251718  | 0.884730  |
| C | -1.490578 | 2.585129  | 0.303328  |
| H | -0.233001 | 1.689620  | 1.816482  |
| H | 0.417984  | 3.170919  | 1.111788  |
| O | -1.786179 | 2.349647  | -0.843987 |
| O | -2.276606 | 3.164566  | 1.198112  |
| H | -3.121865 | 3.401801  | 0.780720  |
| O | 1.110531  | -1.151659 | -1.087618 |
| O | -3.596136 | -0.996103 | -1.354663 |
| H | -4.393831 | -1.383123 | -0.973059 |

TS\_7-8.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.477704 | -2.531918 | 0.997199  |
| C | -0.917776 | -2.196381 | -0.209882 |
| C | -2.498189 | -1.700940 | 1.517706  |
| C | -2.718667 | -0.463158 | 0.916684  |
| H | -3.012329 | -1.965238 | 2.435257  |
| C | -3.117926 | 1.953120  | -0.530210 |
| C | -1.961168 | -0.145758 | -0.280306 |
| C | -3.570278 | 0.556735  | 1.424447  |
| C | -3.748138 | 1.726086  | 0.735234  |
| C | -2.302576 | 0.994164  | -1.075941 |
| H | -0.677694 | 0.192698  | 0.112505  |
| H | -4.101369 | 0.385170  | 2.355653  |
| H | -4.405453 | 2.492391  | 1.138456  |
| H | -1.857276 | 1.134566  | -2.055176 |
| H | -1.064523 | -3.350081 | 1.575559  |
| N | 0.245282  | -2.663382 | -0.755937 |
| H | 0.724120  | -3.368769 | -0.210314 |
| C | 1.095017  | -1.657982 | -1.382936 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 2.009855  | -2.145580 | -1.722286 |
| H | 0.589420  | -1.246636 | -2.259953 |
| C | 1.444398  | -0.490234 | -0.447543 |
| O | 0.601199  | 0.196191  | 0.198809  |
| N | 2.723331  | -0.188389 | -0.325430 |
| H | 3.449066  | -0.718110 | -0.804754 |
| C | 3.197198  | 0.921054  | 0.483759  |
| C | 4.708600  | 0.943570  | 0.371869  |
| H | 2.780641  | 1.869509  | 0.130607  |
| H | 2.901014  | 0.796294  | 1.529942  |
| O | 5.330904  | 0.146324  | -0.285806 |
| O | 5.231776  | 1.935196  | 1.079794  |
| H | 6.198993  | 1.923134  | 0.985037  |
| O | -1.484745 | -1.259708 | -1.008055 |
| O | -3.321316 | 3.088707  | -1.229227 |
| H | -3.974048 | 3.659210  | -0.805580 |

TS\_8-5b.xyz

34

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.765012  | -2.420435 | -0.201748 |
| C | 1.035715  | -1.263314 | -0.517664 |
| C | 3.091705  | -2.292315 | 0.118089  |
| C | 3.699664  | -0.999963 | 0.147529  |
| H | 3.689854  | -3.168906 | 0.345059  |
| C | 4.738541  | 1.605755  | 0.163521  |
| C | 2.904261  | 0.124473  | -0.147705 |
| C | 5.054351  | -0.768939 | 0.454334  |
| C | 5.571477  | 0.509634  | 0.464702  |
| C | 3.389836  | 1.416268  | -0.146188 |
| H | -0.674059 | -0.429163 | -1.314381 |
| H | 5.692964  | -1.615727 | 0.686263  |
| H | 6.617687  | 0.676559  | 0.702268  |
| H | 2.754270  | 2.261130  | -0.383473 |
| H | 1.271156  | -3.384507 | -0.242048 |
| N | -0.304370 | -1.218200 | -0.740087 |
| H | -0.713141 | -2.111573 | -1.003036 |
| C | -1.450144 | -0.576289 | 0.735500  |
| H | -1.703120 | -1.438986 | 1.346498  |
| H | -0.727068 | 0.112941  | 1.162820  |
| C | -2.502998 | 0.056806  | -0.116962 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| O | -2.178536 | 0.563717  | -1.198558 |
| N | -3.768501 | 0.014096  | 0.317438  |
| H | -4.017341 | -0.369159 | 1.224369  |
| C | -4.841812 | 0.621755  | -0.441199 |
| C | -6.125684 | 0.425110  | 0.334161  |
| H | -4.665481 | 1.691956  | -0.594502 |
| H | -4.934552 | 0.164124  | -1.431560 |
| O | -6.181487 | -0.132678 | 1.402958  |
| O | -7.167489 | 0.943312  | -0.309640 |
| H | -7.968447 | 0.802947  | 0.221458  |
| O | 1.571480  | -0.036357 | -0.451442 |
| O | 5.179590  | 2.871672  | 0.155431  |
| H | 6.119381  | 2.928497  | 0.370584  |