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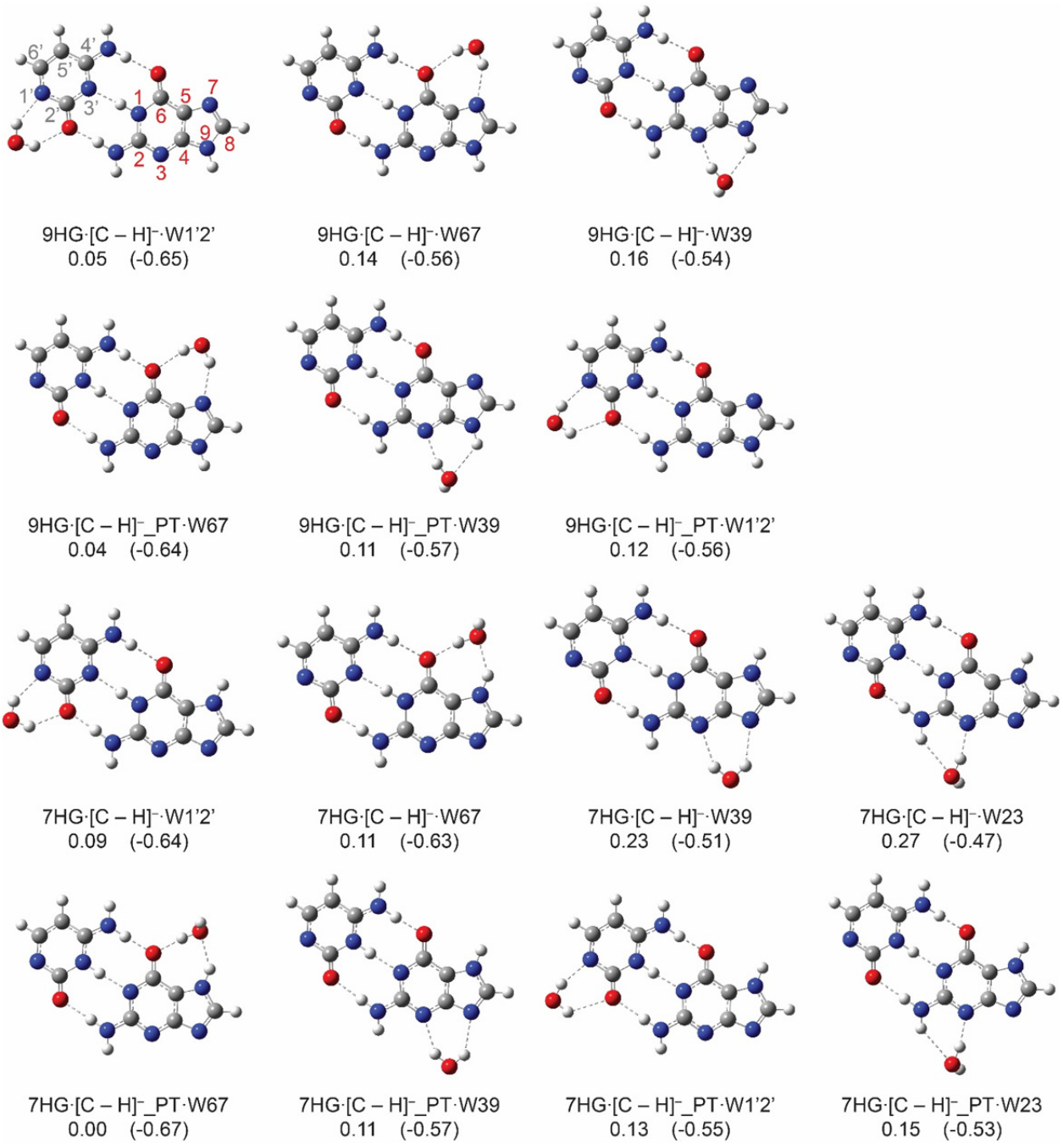

Fig. S1 Conformers and tautomers of low-lying mono-hydrated $[G{\cdot}C - H]^-$, optimized at B3LYP/6-311++G(d,p). Numbering scheme and nomenclature are presented. Dashed lines indicate hydrogen bonds. Relative energies (eV, with thermal corrections at 298 K) were calculated with respect to the global minimum. Hydration energies ($E_{hydration}$ = E(monohydrate) – E(H_2O) – E(bare ion)) are presented in parenthesis.

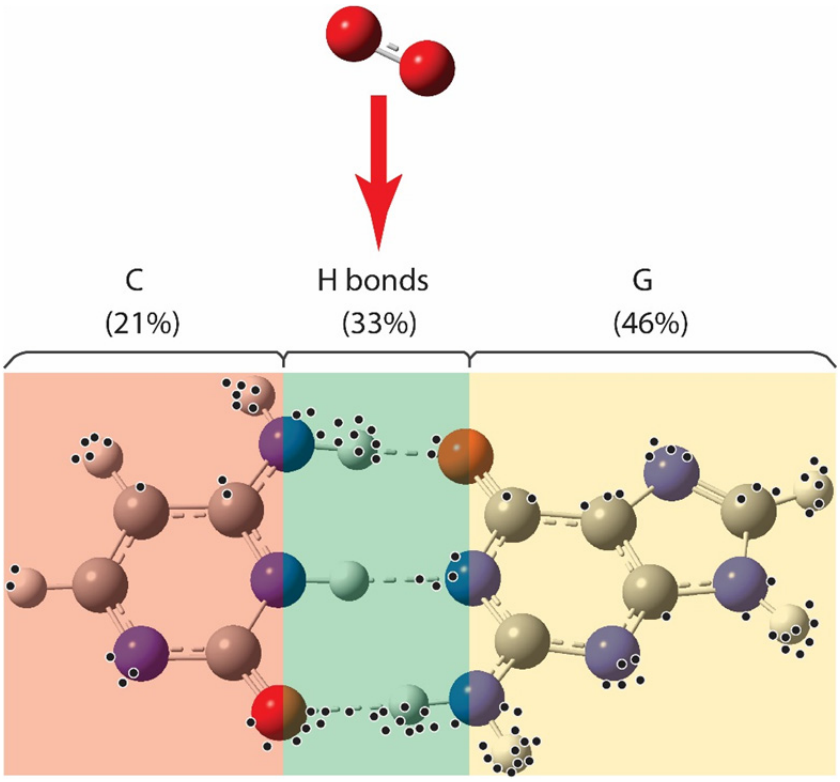

Fig. S2 Collision sites in the trajectories of 9HG·[C – H]⁻_PT + $^1O_2$. Percentages in parenthesis are the collision probabilities sampled at each region.

Oxidation of cytosine Formation of a peroxide of $[C - H]^-$ was observed occasionally in the trajectories. Fig. S3 shows the PESs for the formation of 5′-peroxide of the cytosine residues in 9HG·$[C - H]^-$ and 9HG·$[C - H]^-$_PT, respectively. The oxidation of deprotonated C has an activation energy $\Delta H(TS^{\ddagger}) = 0.31$ eV/$\Delta G(TS^{\ddagger}) = 0.72$ eV, while that of neutral C increases the barrier by 0.2 eV, rendering the $^1O_2$ reactions with cytosine kinetically blocked at low E_{col}. We believe that the oxidation of cytosine in the trajectories is an artifact and due to an issue with using the quasi-classical method in that E_{vib} was not quantized in molecules. Lack of quantization presumably has an effect on how energy was distributed among vibrational modes.[1] It is possible that some trajectories have borrowed ZPE to overcome the activation barrier for cytosine oxidation.

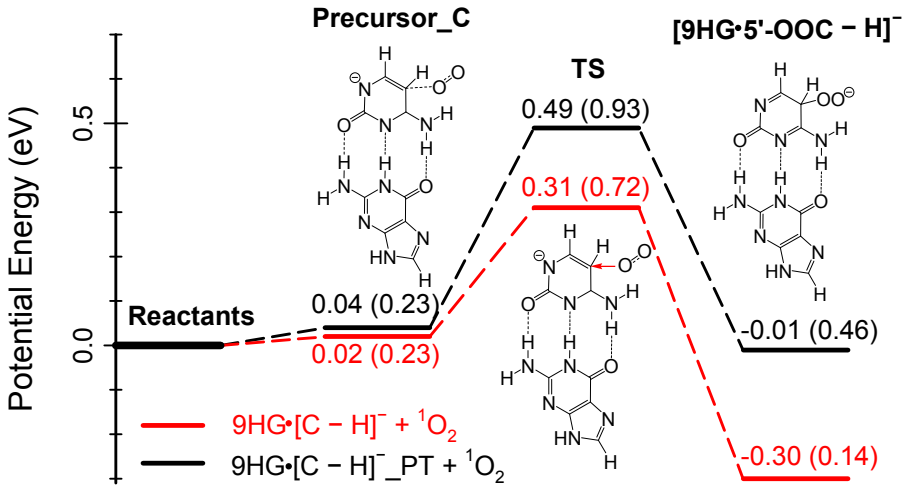

Fig. S3 PESs for the $^1O_2$ oxidation of the cytosine moiety in 9HG·$[C - H]^-$ and 9HG·$[C - H]^-$_PT. All structures were optimized at B3LYP/6-311++G(d,p). Reaction enthalpies (ΔH) and free energy changes (ΔG, presented in parenthesis) were refined by single-point calculations at ωB97XD/6-311++G(d,p) coupled with approximate spin-projection-based corrections for $^1O_2$ and TSs. Depicted structures refer to conventional conformers.

[1] a) A. Untch, R. Schinke, R. Cotting and J. R. Huber, *J. Chem. Phys.*, 1993, **99**, 9553-9566; b) W. H. Miller, W. L. Hase and C. L. Darling, *J. Chem. Phys.*, 1989, **91**, 2863-2868.

Cartesian coordinates for the structures in Scheme 1, optimized at B3LYP/6-311++ G(d,p).

9HG·[C – H]$^-$

C1 -1.414739 -1.002454 -0.034709
C2 -2.825205 -0.726429 -0.062789
H3 0.386777 0.070154 0.085171
C4 -1.173845 1.456555 0.122524
H5 -5.215017 1.359065 -0.012314
C6 -4.956876 -0.780819 -0.133787
N7 -0.661130 0.181794 0.059099
N8 -3.920458 -1.571684 -0.148852
N9 -4.604483 0.558386 -0.040862
N10 -2.484005 1.718399 0.095902
C11 -3.229904 0.607121 0.005689
N12 -0.290683 2.457657 0.229089
H13 -0.680963 3.384718 0.198323
H14 0.751978 2.318475 0.113152
O15 -0.853351 -2.098109 -0.081645
H16 -5.989833 -1.092506 -0.185750
C17 2.954481 1.085897 -0.079124
N18 2.212865 -0.072333 0.093673
C19 2.838829 -1.250412 0.128605
C20 4.900897 -0.134231 -0.194215
N21 4.323020 1.059005 -0.226826
H22 5.986276 -0.137421 -0.315227
O23 2.346979 2.189505 -0.104411
N24 2.070883 -2.370790 0.355332
H25 1.064777 -2.292133 0.201437
H26 2.479148 -3.252353 0.089400
C27 4.237352 -1.342165 -0.021070
H28 4.759834 -2.290598 0.011632

9HG·[C – H]$^-$_TS‡

C1 -1.293986 -0.929678 -0.194231
C2 -2.713208 -0.698074 -0.154338
H3 0.770217 0.087122 -0.002711
C4 -1.092382 1.437330 0.255604
H5 -5.148572 1.298877 0.244545
C6 -4.846382 -0.799500 -0.163512
N7 -0.530116 0.217044 0.018453
N8 -3.793621 -1.554820 -0.313990
N9 -4.521545 0.525618 0.092338
N10 -2.406977 1.697181 0.309221
C11 -3.145797 0.600442 0.100560
N12 -0.239545 2.469980 0.485029
H13 -0.680709 3.375524 0.476368
H14 0.726204 2.403085 0.118404
O15 -0.748702 -2.031680 -0.388384
H16 -5.873668 -1.128760 -0.224028
C17 2.871588 1.066802 -0.303230
N18 2.082637 -0.052162 -0.009252
C19 2.654613 -1.241095 0.260991
C20 4.769867 -0.215872 -0.067445
N21 4.242144 0.967599 -0.340483
H22 5.859872 -0.265644 -0.102387
O23 2.301745 2.152874 -0.528343
N24 1.837832 -2.287623 0.570417
H25 0.860418 -2.247055 0.237105
H26 2.269101 -3.197818 0.555269
C27 4.055111 -1.364704 0.247002
H28 4.540583 -2.308514 0.460714

9HG·[C – H]$^-$_PT

C1 -1.356538 -0.900953 0.055167
C2 -2.781860 -0.718117 -0.038174
H3 1.207817 0.113843 0.087439
C4 -1.227728 1.468940 0.178880
H5 -5.272673 1.252273 -0.147231
C6 -4.907471 -0.874080 -0.211408
N7 -0.625158 0.261710 0.160745
N8 -3.835436 -1.616118 -0.158757
N9 -4.623928 0.482353 -0.132761
N10 -2.547223 1.725151 0.083285
C11 -3.253444 0.593859 -0.019831
N12 -0.410660 2.558900 0.344063
H13 -0.836250 3.444125 0.122948
H14 0.585916 2.458942 0.149690
O15 -0.785155 -2.021583 0.041218
H16 -5.921643 -1.235323 -0.305674
C17 3.046073 1.125022 -0.136498
N18 2.248013 -0.027655 0.023555
C19 2.741129 -1.289758 0.093462
C20 4.878510 -0.271576 -0.161813
N21 4.403876 0.964870 -0.229490
H22 5.963358 -0.357541 -0.240548
O23 2.481919 2.221144 -0.185170
N24 1.874565 -2.298157 0.265745
H25 0.829539 -2.159420 0.194068
H26 2.239137 -3.234862 0.223554
C27 4.135372 -1.437073 -0.004971
H28 4.598077 -2.413474 0.043773

7HG·[C – H]$^-$

C1 -1.398584 -0.946493 -0.043392
C2 -2.788965 -0.652162 -0.064594
H3 0.403368 0.110650 0.084847
C4 -1.189725 1.492995 0.135686
C5 -4.980267 -0.635610 -0.128619
N6 -0.648718 0.219349 0.059666
N7 -3.901331 -1.469001 -0.154316

N8 -4.658158 0.637301 -0.030937
N9 -2.492983 1.749447 0.110926
C10 -3.273606 0.652384 0.011738
N11 -0.303870 2.496014 0.258112
H12 -0.696246 3.421940 0.221549
H13 0.727204 2.356305 0.115826
O14 -0.880011 -2.073537 -0.105331
H15 -5.990947 -1.014253 -0.185087
H16 -3.891672 -2.473907 -0.220747
C17 2.952077 1.076323 -0.099558
N18 2.203006 -0.077227 0.090032
C19 2.821533 -1.257580 0.143725
C20 4.891277 -0.160535 -0.190995
N21 4.322237 1.035068 -0.244176
H22 5.976978 -0.173480 -0.309293
O23 2.352175 2.180124 -0.143297
N24 2.044453 -2.372088 0.384874
H25 1.042626 -2.286857 0.211088
H26 2.448797 -3.255902 0.119209
C27 4.218824 -1.361981 -0.000136
H28 4.734732 -2.313291 0.049244

7HG·[C – H]$^{-}$_TS‡
C1 -1.291206 -0.883626 -0.187144
C2 -2.688354 -0.622735 -0.143344
H3 0.760780 0.105156 0.003720
C4 -1.104913 1.468892 0.262248
C5 -4.882249 -0.642317 -0.133673
N6 -0.526028 0.242888 0.023939
N7 -3.790325 -1.445208 -0.293607
N8 -4.577480 0.615727 0.108288
N9 -2.410299 1.729656 0.313123
C10 -3.190941 0.649352 0.107573
N11 -0.239960 2.494874 0.497022
H12 -0.678247 3.402051 0.486257
H13 0.717808 2.424906 0.118918
O14 -0.792782 -2.018242 -0.387738
H15 -5.888142 -1.031452 -0.205425
H16 -3.764818 -2.432848 -0.488473
C17 2.877093 1.056488 -0.311406
N18 2.079960 -0.055208 -0.007618
C19 2.642558 -1.246016 0.266046
C20 4.765575 -0.241337 -0.069664
N21 4.248263 0.944286 -0.348579
H22 5.855175 -0.300908 -0.104441
O23 2.315420 2.142991 -0.544926
N24 1.816175 -2.287201 0.582780
H25 0.843026 -2.243625 0.244327
H26 2.242318 -3.199845 0.562436
C27 4.040801 -1.383664 0.250635
H28 4.518659 -2.330358 0.468929

7HG·[C – H]$^{-}$_PT
C1 -1.353846 -0.852810 0.055754
C2 -2.758763 -0.642519 -0.034774
H3 1.208754 0.127393 0.088854
C4 -1.244694 1.501931 0.187792
C5 -4.946772 -0.719233 -0.219211
N6 -0.622115 0.290705 0.166651
N7 -3.832423 -1.506712 -0.163064
N8 -4.683447 0.568197 -0.138711
N9 -2.554248 1.756056 0.090040
C10 -3.301200 0.639482 -0.021082
N11 -0.418326 2.587815 0.364088
H12 -0.844098 3.473169 0.142152
H13 0.571705 2.484699 0.147419
O14 -0.825586 -2.007126 0.031786
H15 -5.936560 -1.142484 -0.319561
H16 -3.775355 -2.510932 -0.205931
C17 3.055659 1.116113 -0.150769
N18 2.246036 -0.028531 0.022851
C19 2.726733 -1.293587 0.104122
C20 4.873990 -0.300439 -0.162213
N21 4.412840 0.939081 -0.242394
H22 5.957852 -0.399149 -0.240123
O23 2.502654 2.215163 -0.211532
N24 1.850972 -2.295247 0.288103
H25 0.811037 -2.154032 0.204191
H26 2.210052 -3.234090 0.247643
C27 4.117980 -1.457343 0.006340
H28 4.570525 -2.437991 0.064611

Cartesian coordinates for the structures in Fig. 5, optimized at B3LYP/6-311++G(d,p).

9HG·[C – H]$^-$
Precursor_9H (open shell)
O1 -3.425745 -0.539298 2.194934
O2 -4.597807 -0.822283 2.027590
C3 -0.952181 -0.845170 -0.569860
C4 -2.344110 -0.504628 -0.714336
H5 0.859693 0.121918 -0.129435
C6 -0.649385 1.566711 -0.112109
H7 -4.659726 1.664512 -0.660078
C8 -4.451195 -0.450877 -1.022458
N9 -0.175573 0.284206 -0.260890
N10 -3.443102 -1.280961 -1.022369
N11 -4.068716 0.853381 -0.746950
N12 -1.941171 1.891464 -0.250940
C13 -2.709952 0.836093 -0.539385
N14 0.246731 2.509642 0.193411
H15 -0.111028 3.449232 0.240973
H16 1.294280 2.335412 0.188761
O17 -0.429575 -1.953153 -0.687312
H18 -5.480419 -0.709609 -1.221226
C19 3.446062 1.029989 0.130845
N20 2.653017 -0.105019 0.077967
C21 3.233022 -1.307394 0.065555
C22 5.352214 -0.255789 0.135611
N23 4.819607 0.958730 0.158576
H24 6.443312 -0.294012 0.155820
O25 2.880950 2.156939 0.149653
N26 2.408711 -2.409577 0.067425
H27 1.434133 -2.272749 -0.201671
H28 2.821723 -3.278786 -0.229489
C29 4.635380 -1.444474 0.089188
H30 5.119777 -2.413369 0.085500

TS1_9H (open shell)
O1 -4.597561 0.223000 1.863070
O2 -5.086477 -0.685717 1.074262
C3 -0.850463 -0.959427 -0.268778
C4 -2.261037 -0.653132 -0.400878
H5 0.989654 0.062357 -0.164041
C6 -0.532821 1.481972 -0.323732
H7 -4.550674 1.519652 -0.446778
C8 -4.424291 -0.611540 -0.490378
N9 -0.059651 0.199763 -0.242634
N10 -3.323908 -1.464926 -0.482622
N11 -3.989429 0.720529 -0.701954
N12 -1.846189 1.780720 -0.470526
C13 -2.627920 0.722000 -0.504291
N14 0.352289 2.467039 -0.263897
H15 -0.031354 3.397683 -0.309306
H16 1.408102 2.308312 -0.101062
O17 -0.336917 -2.072449 -0.189172
H18 -5.311202 -0.940143 -1.023587
C19 3.505717 1.051966 0.179469
N20 2.765722 -0.097335 -0.034999
C21 3.383755 -1.282436 -0.027614
C22 5.428042 -0.179082 0.424417
N23 4.856734 1.018635 0.414578
H24 6.502470 -0.188486 0.615903
O25 2.906440 2.165223 0.159267
N26 2.625679 -2.395618 -0.301213
H27 1.611753 -2.313383 -0.240418
H28 3.010038 -3.284988 -0.027622
C29 4.768086 -1.381841 0.212334
H30 5.284193 -2.333993 0.217065

8-OOG·[C – H]$^-$
O1 -3.441652 0.219957 1.643129
O2 -4.584417 -0.498891 1.224333
C3 -0.922890 -0.993134 -0.227115
C4 -2.369049 -0.707641 -0.341382
H5 0.893024 0.048714 -0.135750
C6 -0.665282 1.450890 -0.296033
H7 -4.648715 1.461441 -0.467393
C8 -4.495682 -0.637672 -0.225413
N9 -0.161881 0.165243 -0.196756
N10 -3.370055 -1.519044 -0.447883
N11 -4.098996 0.664739 -0.766015
N12 -1.971732 1.747514 -0.462741
C13 -2.772388 0.703387 -0.424839
N14 0.218455 2.427033 -0.242483
H15 -0.167693 3.356774 -0.304601
H16 1.288553 2.275536 -0.102026
O17 -0.416790 -2.101996 -0.179779
H18 -5.454681 -1.010485 -0.572282
C19 3.389251 1.071743 0.122472
N20 2.667104 -0.092920 -0.063334
C21 3.310937 -1.264594 -0.064724
C22 5.342053 -0.115232 0.325516
N23 4.744736 1.069768 0.321474
H24 6.420830 -0.100141 0.488629
O25 2.766149 2.173398 0.109387
N26 2.571215 -2.396216 -0.312771
H27 1.558954 -2.333933 -0.233674
H28 2.978786 -3.275478 -0.040314
C29 4.702154 -1.332920 0.139448
H30 5.238073 -2.273958 0.136828

TS2_9H
O1 -3.413758 0.445777 1.455031

O2 -4.564321 -0.370240 1.215569
C3 -0.905312 -1.020078 -0.161578
C4 -2.362609 -0.766017 -0.278573
H5 0.882740 0.051872 -0.108315
C6 -0.710428 1.430661 -0.289664
H7 -4.694522 1.330633 -0.648577
C8 -4.491830 -0.697451 -0.204037
N9 -0.173882 0.148177 -0.155165
N10 -3.344811 -1.594303 -0.334042
N11 -4.101131 0.538015 -0.871975
N12 -2.008061 1.701761 -0.443788
C13 -2.814870 0.643194 -0.329410
N14 0.176879 2.412115 -0.284588
H15 -0.209931 3.340206 -0.356857
H16 1.235412 2.270201 -0.143853
O17 -0.389043 -2.124476 -0.097508
H18 -5.447288 -1.122559 -0.495196
C19 3.382731 1.087283 0.105163
N20 2.670316 -0.088225 -0.062715
C21 3.326867 -1.251985 -0.063741
C22 5.350409 -0.080436 0.298222
N23 4.741979 1.098132 0.292490
H24 6.430713 -0.054210 0.451070
O25 2.749341 2.179925 0.086723
N26 2.596367 -2.394536 -0.297097
H27 1.585580 -2.340012 -0.198100
H28 3.015607 -3.265274 -0.014535
C29 4.720772 -1.305993 0.125585
H30 5.265977 -2.241762 0.122197

4,8-OO-G·[C – H]$^-$
O1 -3.481455 0.399441 1.333919
O2 -4.605216 -0.495030 1.041869
C3 -0.880617 -0.997755 -0.261708
C4 -2.344957 -0.750826 -0.352264
H5 0.881205 0.074924 -0.019116
C6 -0.740383 1.453523 -0.029610
H7 -4.701815 1.342929 -0.634989
C8 -4.477950 -0.688958 -0.397639
N9 -0.174546 0.163863 -0.088172
N10 -3.303404 -1.568540 -0.578473
N11 -4.059879 0.602761 -0.910083
N12 -2.028729 1.725181 -0.067075
C13 -2.860980 0.636487 -0.089326
N14 0.159008 2.429987 0.061295
H15 -0.219839 3.362521 0.101142
H16 1.211230 2.281638 -0.011299
O17 -0.358656 -2.099810 -0.346909
H18 -5.416302 -1.096500 -0.762165
C19 3.403850 1.082505 -0.059779
N20 2.671196 -0.087494 0.069502
C21 3.317187 -1.251680 0.170991
C22 5.375226 -0.097626 -0.002778
N23 4.777675 1.081676 -0.100498
H24 6.466144 -0.079701 -0.037911
O25 2.778892 2.173656 -0.145629
N26 2.557012 -2.387385 0.349486
H27 1.572747 -2.332476 0.099083
H28 3.005814 -3.263057 0.134241
C29 4.722842 -1.316232 0.136739
H30 5.258675 -2.253298 0.225364

TS3_9H
O1 -4.859211 0.308962 1.646435
O2 -5.246007 -0.713105 0.698391
C3 -0.799263 -0.977933 -0.189349
C4 -2.243810 -0.672089 -0.335217
H5 1.039245 0.038255 -0.125085
C6 -0.510135 1.455291 -0.271568
H7 -4.460594 1.263893 0.226446
C8 -4.442259 -0.618804 -0.447878
N9 -0.019862 0.166012 -0.194443
N10 -3.238842 -1.478804 -0.365338
N11 -3.984902 0.775015 -0.584717
N12 -1.826384 1.767218 -0.411229
C13 -2.641548 0.742621 -0.457267
N14 0.373276 2.423916 -0.212511
H15 -0.016190 3.354003 -0.268295
H16 1.467775 2.264828 -0.079834
O17 -0.316120 -2.093303 -0.094044
H18 -5.038223 -0.957247 -1.301494
C19 3.506666 1.057459 0.135337
N20 2.778967 -0.105491 -0.020541
C21 3.419313 -1.280842 -0.000402
C22 5.456145 -0.127303 0.345347
N23 4.860139 1.058898 0.320947
H24 6.535962 -0.110295 0.497507
O25 2.886080 2.164619 0.106483
N26 2.674689 -2.413836 -0.213364
H27 1.663070 -2.351621 -0.134320
H28 3.086373 -3.292191 0.054813
C29 4.811564 -1.346544 0.193015
H30 5.345044 -2.288636 0.208395

8-OOHG·[C – H]$^-$
O1 -5.087737 -0.250433 1.688422
O2 -5.458412 -0.712580 0.363209
C3 -0.779092 -0.891853 -0.183255
C4 -2.230610 -0.569969 -0.297656
H5 1.053361 0.101276 -0.122774
C6 -0.496527 1.547263 -0.261011
H7 -4.998748 0.705518 1.524195

C8 -4.385382 -0.464403 -0.517623
N9 -0.001362 0.239892 -0.173047
N10 -3.221523 -1.370170 -0.303455
N11 -3.954096 0.916682 -0.500027
N12 -1.779333 1.881553 -0.381358
C13 -2.655308 0.862618 -0.408094
N14 0.432356 2.490990 -0.220408
H15 0.083515 3.435674 -0.270554
H16 1.478660 2.301681 -0.057094
O17 -0.317173 -2.020273 -0.117758
H18 -4.813317 -0.737679 -1.492427
C19 3.572402 1.016572 0.197347
N20 2.817269 -0.121982 -0.031337
C21 3.427314 -1.310504 -0.067999
C22 5.488855 -0.236202 0.372027
N23 4.927314 0.964769 0.406494
H24 6.566500 -0.259492 0.542474
O25 2.982649 2.132919 0.215392
N26 2.655256 -2.413368 -0.354980
H27 1.647630 -2.324127 -0.251150
H28 3.039111 -3.309941 -0.104273
C29 4.814284 -1.427652 0.139127
H30 5.321891 -2.383735 0.107145

9HG·[C – H]$^-$_PT
Precursor_9H_PT (open shell)
O1 -3.569822 -0.420990 2.151332
O2 -4.718919 -0.769010 1.915901
C3 -0.888956 -0.773226 -0.448434
C4 -2.297359 -0.524502 -0.651983
H5 1.688147 0.117427 -0.027924
C6 -0.694106 1.568901 -0.109693
H7 -4.707603 1.543846 -0.781669
C8 -4.394308 -0.571590 -1.040831
N9 -0.134023 0.343538 -0.173310
N10 -3.353180 -1.359087 -0.961431
N11 -4.076064 0.761040 -0.829537
N12 -1.993092 1.890166 -0.307547
C13 -2.725089 0.808076 -0.564908
N14 0.134835 2.604158 0.210522
H15 -0.244522 3.527113 0.083519
H16 1.146985 2.479356 0.163673
O17 -0.360935 -1.909409 -0.517427
H18 -5.403994 -0.883877 -1.262650
C19 3.563634 1.070635 0.105669
N20 2.722140 -0.059441 0.032186
C21 3.168439 -1.340583 0.033506
C22 5.344958 -0.387609 0.182257
N23 4.915792 0.867209 0.182277
H24 6.427464 -0.508063 0.243812
O25 3.038797 2.187685 0.096889
N26 2.261175 -2.326261 -0.024396
H27 1.241024 -2.139864 -0.202543
H28 2.600576 -3.269574 -0.105614
C29 4.558001 -1.532661 0.110594
H30 4.984590 -2.526459 0.117431

TS1_9H_PT (open shell)
O1 -4.671982 0.120976 1.875659
O2 -5.032449 -0.841927 1.075822
C3 -0.799687 -0.828310 -0.356402
C4 -2.234095 -0.603128 -0.454370
H5 1.792886 0.091515 -0.097277
C6 -0.588959 1.526791 -0.288424
H7 -4.620149 1.439727 -0.275438
C8 -4.400037 -0.656108 -0.504496
N9 -0.027892 0.307938 -0.275324
N10 -3.262603 -1.456732 -0.555176
N11 -4.038960 0.706024 -0.655612
N12 -1.920164 1.830212 -0.398491
C13 -2.668620 0.755620 -0.477556
N14 0.236682 2.592273 -0.198649
H15 -0.187616 3.502630 -0.158398
H16 1.245014 2.477463 -0.065561
O17 -0.278716 -1.964118 -0.346361
H18 -5.281417 -1.001846 -1.036330
C19 3.628529 1.078233 0.185647
N20 2.822499 -0.066896 0.020096
C21 3.296961 -1.337669 0.020825
C22 5.430964 -0.342172 0.363776
N23 4.973539 0.902814 0.359985
H24 6.507562 -0.440616 0.507303
O25 3.077458 2.183669 0.164639
N26 2.423052 -2.338317 -0.164807
H27 1.392424 -2.176543 -0.232747
H28 2.762464 -3.282588 -0.101144
C29 4.678813 -1.502248 0.204619
H30 5.128075 -2.485809 0.215655

8-OOG·[C – H]$^-$_PT
O1 -3.507542 0.080138 1.701405
O2 -4.602911 -0.666240 1.193968
C3 -0.875582 -0.860114 -0.322944
C4 -2.343768 -0.655197 -0.394985
H5 1.700669 0.079024 -0.104051
C6 -0.718846 1.494397 -0.248804
H7 -4.713678 1.411776 -0.319191
C8 -4.479235 -0.690691 -0.252898
N9 -0.129565 0.276080 -0.233761
N10 -3.312842 -1.500877 -0.535132
N11 -4.145311 0.666662 -0.703238
N12 -2.044090 1.800082 -0.380689

C13 -2.809931 0.736838 -0.400405
N14 0.100894 2.550667 -0.145451
H15 -0.323505 3.462726 -0.138795
H16 1.116305 2.440847 -0.052856
O17 -0.359785 -1.987230 -0.355475
H18 -5.414110 -1.082600 -0.645000
C19 3.520358 1.104430 0.112847
N20 2.734945 -0.059346 -0.016401
C21 3.235887 -1.319305 -0.007739
C22 5.355101 -0.275226 0.269705
N23 4.871766 0.959592 0.257036
H24 6.436396 -0.349300 0.389164
O25 2.944430 2.197316 0.088573
N26 2.378450 -2.341472 -0.157586
H27 1.351180 -2.199284 -0.224946
H28 2.735013 -3.278964 -0.091297
C29 4.623520 -1.453273 0.145961
H30 5.093437 -2.426974 0.161333

TS2_9H_PT
O1 -3.459483 0.373064 1.453338
O2 -4.571267 -0.500225 1.182453
C3 -0.859018 -0.900315 -0.237730
C4 -2.337445 -0.732366 -0.322416
H5 1.695849 0.079731 -0.073307
C6 -0.776038 1.465456 -0.214548
H7 -4.768907 1.270171 -0.571675
C8 -4.472596 -0.760128 -0.248496
N9 -0.147982 0.245181 -0.168995
N10 -3.284315 -1.597334 -0.424035
N11 -4.138623 0.525016 -0.852609
N12 -2.085275 1.742623 -0.325200
C13 -2.861866 0.654123 -0.266463
N14 0.054656 2.523607 -0.168632
H15 -0.366074 3.437054 -0.174267
H16 1.069304 2.415759 -0.098098
O17 -0.332500 -2.027341 -0.248213
H18 -5.406989 -1.214637 -0.565484
C19 3.512879 1.125909 0.067972
N20 2.733906 -0.048041 -0.008927
C21 3.247622 -1.302816 0.015006
C22 5.364582 -0.234275 0.208537
N23 4.869964 0.995371 0.179971
H24 6.449493 -0.296567 0.300233
O25 2.928038 2.212344 0.029901
N26 2.397818 -2.337075 -0.082680
H27 1.366216 -2.208514 -0.139996
H28 2.770133 -3.268788 -0.022494
C29 4.640586 -1.420955 0.132350
H30 5.119398 -2.390189 0.157735

4,8-OO-G·[C – H]⁻_PT
O1 -3.550003 0.467838 1.304164
O2 -4.633943 -0.487403 1.051314
C3 -0.843438 -0.907374 -0.165183
C4 -2.323139 -0.753849 -0.281519
H5 1.701778 0.084943 0.001289
C6 -0.798815 1.464249 -0.101761
H7 -4.756279 1.220980 -0.736851
C8 -4.458322 -0.780145 -0.367812
N9 -0.150464 0.239659 -0.075203
N10 -3.249845 -1.620915 -0.467473
N11 -4.082492 0.492027 -0.961743
N12 -2.096816 1.734188 -0.160592
C13 -2.897499 0.625387 -0.127772
N14 0.044253 2.519448 -0.072732
H15 -0.368266 3.436283 -0.080845
H16 1.058769 2.406147 -0.063061
O17 -0.313440 -2.036098 -0.174539
H18 -5.373257 -1.247566 -0.722006
C19 3.525562 1.131116 0.002330
N20 2.741738 -0.042789 0.026610
C21 3.255395 -1.296998 0.073309
C22 5.381938 -0.229231 0.074487
N23 4.887712 0.999742 0.029167
H24 6.470625 -0.291853 0.094134
O25 2.941377 2.216714 -0.042198
N26 2.400589 -2.331679 0.105082
H27 1.370661 -2.206263 0.002636
H28 2.780833 -3.261868 0.075291
C29 4.653168 -1.415262 0.097337
H30 5.131389 -2.384337 0.137184

TS3_9H_PT
O1 -4.848903 0.119595 1.712307
O2 -5.228833 -0.839723 0.690355
C3 -0.766510 -0.842948 -0.288741
C4 -2.235392 -0.616409 -0.386587
H5 1.826214 0.060950 -0.086234
C6 -0.581653 1.505529 -0.229398
H7 -4.531579 1.231424 0.260012
C8 -4.442683 -0.652588 -0.451901
N9 -0.005842 0.285067 -0.225793
N10 -3.199843 -1.459533 -0.439848
N11 -4.044165 0.765101 -0.538840
N12 -1.914207 1.825371 -0.334987
C13 -2.696394 0.782847 -0.422905
N14 0.239078 2.556469 -0.127608
H15 -0.182245 3.470630 -0.123392
H16 1.257296 2.441344 -0.046781
O17 -0.268923 -1.976136 -0.281513
H18 -5.036648 -0.974793 -1.314278

C19 3.641521 1.085792 0.124183
N20 2.856447 -0.079685 0.011563
C21 3.355017 -1.340055 0.046240
C22 5.473367 -0.292298 0.309881
N23 4.991143 0.942503 0.273841
H24 6.554063 -0.365000 0.433000
O25 3.063895 2.177826 0.081301
N26 2.494376 -2.363334 -0.086114
H27 1.471291 -2.218398 -0.152446
H28 2.845763 -3.301200 -0.000659
C29 4.740855 -1.472445 0.206474
H30 5.210282 -2.445714 0.242213

8-OOHG·[C – H]$^-$_PT
O1 -5.107794 -0.400758 1.662856
O2 -5.444694 -0.821935 0.313623
C3 -0.744543 -0.764951 -0.258630
C4 -2.216644 -0.517274 -0.346093
H5 1.853805 0.082471 -0.061662
C6 -0.554577 1.588519 -0.174039
H7 -4.968520 0.553481 1.514143
C8 -4.378545 -0.474922 -0.547969
N9 0.021563 0.341325 -0.176031
N10 -3.182657 -1.349317 -0.402737
N11 -4.001982 0.917140 -0.427533
N12 -1.849983 1.935853 -0.257289
C13 -2.697331 0.901183 -0.349195
N14 0.322336 2.604771 -0.077812
H15 -0.057622 3.536281 -0.071020
H16 1.330788 2.449058 -0.000223
O17 -0.276515 -1.917097 -0.270753
H18 -4.802067 -0.692790 -1.538860
C19 3.710036 1.040577 0.152367
N20 2.882614 -0.094572 0.019240
C21 3.340264 -1.370946 0.007682
C22 5.497851 -0.404088 0.270892
N23 5.057777 0.846353 0.279554
H24 6.577303 -0.517270 0.376043
O25 3.172509 2.151897 0.147233
N26 2.447018 -2.362525 -0.140812
H27 1.423240 -2.186256 -0.186034
H28 2.775008 -3.311667 -0.096028
C29 4.724061 -1.554619 0.142255
H30 5.159776 -2.544230 0.140271

7HG·[C – H]$^-$
Precursor_7H (open shell)
O1 -4.171742 -1.250957 2.199971
O2 -3.119851 -0.642122 2.289865
C3 -1.003829 -0.752725 -0.496562
C4 -2.373750 -0.376694 -0.601145
H5 0.846424 0.194836 -0.239658
C6 -0.665844 1.665773 -0.264791
H7 -3.568766 -2.122970 -0.843668
C8 -4.543837 -0.220206 -0.852582
N9 -0.197108 0.363584 -0.315504
N10 -3.514370 -1.117397 -0.817405
N11 -4.157466 1.028885 -0.709508
N12 -1.949961 2.001829 -0.381262
C13 -2.783493 0.959929 -0.550475
N14 0.263956 2.615726 -0.100406
H15 -0.087993 3.553767 -0.005369
H16 1.274023 2.397531 0.110182
O17 -0.550422 -1.905303 -0.557932
H18 -5.566748 -0.538916 -0.991589
C19 3.391670 0.984535 0.317899
N20 2.618368 -0.087574 -0.104567
C21 3.192680 -1.279144 -0.279506
C22 5.262346 -0.352707 0.396501
N23 4.737825 0.851230 0.575529
H24 6.330224 -0.439589 0.607664
O25 2.835067 2.102600 0.469544
N26 2.400121 -2.303081 -0.753706
H27 1.389957 -2.189828 -0.672062
H28 2.741264 -3.237492 -0.594641
C29 4.564536 -1.476564 -0.029441
H30 5.044784 -2.436690 -0.174029

TS1_7H
O1 -4.265739 -0.902551 1.377448
O2 -2.967577 -0.589677 1.466080
C3 -0.993419 -0.808921 -0.291506
C4 -2.422504 -0.468835 -0.268531
H5 0.848552 0.138300 -0.017397
C6 -0.688967 1.603108 -0.036328
H7 -3.565102 -2.133612 -0.620449
C8 -4.525960 -0.289302 -0.611129
N9 -0.204684 0.295324 -0.082168
N10 -3.455048 -1.157950 -0.869989
N11 -4.153322 0.992818 -0.535113
N12 -1.974388 1.948625 -0.174935
C13 -2.821551 0.935861 -0.337287
N14 0.228723 2.540119 0.146523
H15 -0.120260 3.485923 0.151018
H16 1.284014 2.344395 0.159513
O17 -0.550344 -1.938865 -0.465264
H18 -5.542773 -0.599903 -0.800120
C19 3.387858 1.024984 0.071301
N20 2.597740 -0.113244 0.058883
C21 3.184894 -1.313209 0.024058
C22 5.297420 -0.248396 -0.014218
N23 4.758234 0.962312 0.030894

H24 6.387847 -0.279538 -0.047397
O25 2.818008 2.150118 0.116994
N26 2.371159 -2.421551 0.072328
H27 1.383201 -2.297362 -0.134033
H28 2.774644 -3.293802 -0.227474
C29 4.585791 -1.441071 -0.020920
H30 5.074828 -2.407098 -0.043332

5,8-OO-G·[C – H]$^-$
O1 -4.438306 -0.689252 1.126906
O2 -2.976137 -0.707358 1.361803
C3 -0.982290 -0.806143 -0.043263
C4 -2.458719 -0.489641 -0.008334
H5 0.858075 0.154881 -0.077719
C6 -0.688113 1.620717 -0.174257
H7 -3.451561 -2.172490 -0.558312
C8 -4.504163 -0.397195 -0.322299
N9 -0.197944 0.305782 -0.071567
N10 -3.386484 -1.199134 -0.853726
N11 -4.133673 0.982942 -0.532668
N12 -1.962582 1.957812 -0.318371
C13 -2.846342 0.947215 -0.333607
N14 0.252609 2.554211 -0.137531
H15 -0.080612 3.502294 -0.215928
H16 1.292430 2.350427 0.008625
O17 -0.553435 -1.950914 -0.046089
H18 -5.501692 -0.681530 -0.647048
C19 3.391716 1.018921 0.158340
N20 2.611536 -0.102465 -0.078498
C21 3.202442 -1.295896 -0.183510
C22 5.296276 -0.265146 0.203340
N23 4.754537 0.940420 0.306123
H24 6.380009 -0.308777 0.325013
O25 2.819594 2.139401 0.242548
N26 2.402246 -2.379194 -0.475053
H27 1.403222 -2.279404 -0.314918
H28 2.783522 -3.286849 -0.262467
C29 4.594937 -1.438920 -0.042691
H30 5.086707 -2.399665 -0.131867

7HG·[C – H]$^-$_PT
Precursor_7H_PT (open shell)
O1 -3.970011 -1.406161 2.171263
O2 -2.936803 -0.756451 2.233626
C3 -0.971743 -0.621227 -0.585776
C4 -2.370416 -0.335426 -0.609671
H5 1.627747 0.179343 -0.190048
C6 -0.737336 1.705372 -0.271673
H7 -3.488007 -2.126799 -0.865997
C8 -4.560414 -0.279290 -0.735887
N9 -0.180339 0.470869 -0.398200
N10 -3.483520 -1.121424 -0.807547
N11 -4.231067 0.979786 -0.549810
N12 -2.040185 2.032075 -0.294564
C13 -2.844908 0.973021 -0.468492
N14 0.145167 2.741792 -0.135391
H15 -0.259471 3.617670 0.150659
H16 1.113666 2.549820 0.117843
O17 -0.507770 -1.790170 -0.727792
H18 -5.572005 -0.646057 -0.835864
C19 3.483840 1.012782 0.355262
N20 2.644745 -0.045249 -0.058959
C21 3.072645 -1.312534 -0.279485
C22 5.224627 -0.496403 0.327891
N23 4.814886 0.744951 0.544430
H24 6.289393 -0.669379 0.490840
O25 2.976608 2.122945 0.525701
N26 2.175339 -2.224187 -0.689467
H27 1.144524 -2.028480 -0.706638
H28 2.481866 -3.180042 -0.753093
C29 4.437428 -1.571102 -0.076899
H30 4.848573 -2.558837 -0.235154

TS1_7H_PT
O1 -4.216119 -0.877579 1.512923
O2 -2.924574 -0.516323 1.528314
C3 -0.964526 -0.729009 -0.238503
C4 -2.415467 -0.472750 -0.208387
H5 1.636564 0.116660 -0.070384
C6 -0.756632 1.612136 -0.144099
H7 -3.508175 -2.195331 -0.420910
C8 -4.527314 -0.397493 -0.587994
N9 -0.188426 0.369557 -0.130970
N10 -3.427429 -1.243609 -0.757370
N11 -4.210511 0.896040 -0.586133
N12 -2.058095 1.947202 -0.299656
C13 -2.870810 0.903500 -0.383003
N14 0.102032 2.639165 -0.010151
H15 -0.287351 3.566384 -0.028864
H16 1.110527 2.493602 0.079733
O17 -0.510895 -1.887070 -0.344279
H18 -5.532187 -0.763052 -0.740732
C19 3.499095 1.066217 0.134502
N20 2.667644 -0.062307 -0.027752
C21 3.122819 -1.336514 -0.106479
C22 5.287343 -0.383213 0.147084
N23 4.849754 0.865736 0.220082
H24 6.368885 -0.501475 0.221218
O25 2.963266 2.176575 0.190263
N26 2.225094 -2.321001 -0.279653
H27 1.200689 -2.145525 -0.296404
H28 2.553357 -3.271042 -0.273029

C29 4.508934 -1.527012 -0.012799
H30 4.943178 -2.515695 -0.069099

5,8-OO-G·[C – H]⁻_PT
O1 -4.424300 -0.819388 1.073916
O2 -2.959507 -0.798582 1.306114
C3 -0.951696 -0.701788 -0.099979
C4 -2.448266 -0.471963 -0.047710
H5 1.650971 0.122595 -0.048623
C6 -0.755180 1.645613 -0.080717
H7 -3.379971 -2.154051 -0.693217
C8 -4.501391 -0.439216 -0.355514
N9 -0.181828 0.390017 -0.066543
N10 -3.355159 -1.164161 -0.934664
N11 -4.186807 0.964132 -0.481539
N12 -2.040697 1.992505 -0.210922
C13 -2.895731 0.962835 -0.282448
N14 0.130146 2.653990 0.030056
H15 -0.238208 3.589318 -0.008638
H16 1.137608 2.490345 0.083175
O17 -0.514407 -1.866694 -0.168635
H18 -5.488597 -0.741876 -0.696883
C19 3.525224 1.059791 0.097093
N20 2.680961 -0.065054 -0.024504
C21 3.125120 -1.343846 -0.092196
C22 5.302688 -0.403317 0.087300
N23 4.876417 0.849767 0.151035
H24 6.384929 -0.528880 0.134776
O25 2.999572 2.174609 0.148472
N26 2.216691 -2.325221 -0.222907
H27 1.193900 -2.142978 -0.201983
H28 2.539209 -3.277152 -0.208138
C29 4.511654 -1.543478 -0.032021
H30 4.936701 -2.536475 -0.082336

Cartesian coordinates for the mono-hydrated structures in Fig. S1, optimized at B3LYP/6-311++G(d,p).

9HG·[C – H]⁻·W1′2′

C1 -1.849849 -0.879460 0.012545
C2 -3.230723 -0.486698 -0.074926
H3 0.812017 -0.264418 0.102094
C4 -1.374355 1.438577 0.228671
H5 -5.405233 1.830106 -0.107204
C6 -5.354372 -0.322489 -0.254167
N7 -0.954755 0.156686 0.162575
N8 -4.403452 -1.215420 -0.230388
N9 -4.875874 0.973645 -0.122630
N10 -2.640279 1.888208 0.143133
C11 -3.505108 0.878512 -0.005068
N12 -0.407738 2.389300 0.437802
H13 -0.696959 3.336732 0.258383
H14 0.564142 2.151956 0.245403
O15 -1.450124 -2.072206 -0.042931
H16 -6.409908 -0.527096 -0.362658
C17 2.791673 0.448303 -0.040819
N18 1.823864 -0.564008 0.054341
C19 2.117373 -1.889641 0.095114
C20 4.397347 -1.214612 -0.056961
N21 4.110880 0.083377 -0.096905
H22 5.458102 -1.458950 -0.104643
O23 2.416872 1.626630 -0.070308
N24 1.105475 -2.755897 0.199212
H25 0.089341 -2.454652 0.119834
H26 1.326360 -3.736762 0.159134
C27 3.478495 -2.248035 0.035733
H28 3.781565 -3.285607 0.063783
O29 5.265429 2.763310 -0.304344
H30 5.154032 1.795188 -0.246862
H31 4.339399 3.033666 -0.257304

9HG·[C – H]⁻·W67

C1 1.294563 0.558493 -0.013215
C2 2.661529 0.123095 -0.019372
H3 -0.626618 -0.285586 0.063274
C4 0.765493 -1.849631 0.094083
H5 4.798615 -2.220576 0.044314
C6 4.790759 -0.068489 -0.045401
N7 0.405795 -0.520187 0.044493
N8 3.850702 0.835758 -0.068101
N9 4.283038 -1.355530 0.016695
N10 2.038526 -2.262310 0.089394
C11 2.910134 -1.248151 0.034087
N12 -0.228841 -2.738954 0.160562
H13 0.051248 -3.705384 0.133370
H14 -1.251295 -2.474790 0.032014
O15 0.869874 1.720863 -0.050266
H16 5.852469 0.125656 -0.071009
C17 -3.270263 -0.997305 -0.123730
N18 -2.402522 0.063598 0.082160
C19 -2.895927 1.301035 0.176665
C20 -5.071096 0.431235 -0.158236
N21 -4.627284 -0.815288 -0.249435
H22 -6.150546 0.557609 -0.262424
O23 -2.788922 -2.160407 -0.200165
N24 -2.008081 2.319846 0.436649
H25 -1.019983 2.139943 0.263414
H26 -2.320940 3.253562 0.225566
C27 -4.277084 1.550445 0.054991
H28 -4.691200 2.548084 0.134852
O29 3.039806 3.728406 -0.223118
H30 3.602781 2.939425 -0.183537
H31 2.161423 3.318258 -0.177581

9HG·[C – H]⁻·W39

C1 0.926741 -1.384433 0.041623
C2 2.361980 -1.301755 0.063977
H3 -0.718615 -0.080499 -0.078141
C4 1.006338 1.088012 -0.120976
H5 4.988368 0.482496 0.017668
C6 4.468458 -1.629266 0.129936
N7 0.336240 -0.107842 -0.051958
N8 3.337672 -2.282230 0.148028
N9 4.296642 -0.258372 0.036445
N10 2.342603 1.166507 -0.095092
C11 2.943640 -0.039031 -0.005604
N12 0.263598 2.194569 -0.228502
H13 0.765251 3.066798 -0.225351
H14 -0.794501 2.192387 -0.111207
O15 0.221423 -2.391438 0.092684
H16 5.451537 -2.073756 0.179091
C17 -3.115827 1.268537 0.081684
N18 -2.538658 0.020887 -0.087557
C19 -3.320425 -1.060655 -0.127976
C20 -5.211109 0.328570 0.183459
N21 -4.474164 1.430973 0.221359
H22 -6.287059 0.475112 0.297771
O23 -2.361966 2.279686 0.111427
N24 -2.712031 -2.274817 -0.350587
H25 -1.705543 -2.335341 -0.193443
H26 -3.239545 -3.093926 -0.095470
C27 -4.718918 -0.958814 0.012980
H28 -5.366473 -1.826387 -0.024093
O29 4.692791 2.666643 -0.078699
H30 4.729308 3.288627 0.653133
H31 3.750714 2.370653 -0.122826

9HG·[C – H]⁻_PT·W67

C1 1.250779 0.478166 0.067942
C2 2.647701 0.145754 -0.008711
H3 -1.427556 -0.237455 0.076410
C4 0.863232 -1.859678 0.148046
H5 4.915704 -2.077545 -0.119911
C6 4.784470 0.071576 -0.151560
N7 0.397006 -0.591150 0.143595
N8 3.796768 0.923927 -0.100282
N9 4.352507 -1.243028 -0.099462
N10 2.149709 -2.255590 0.066603
C11 2.975724 -1.208975 -0.006601
N12 -0.068733 -2.851993 0.277811
H13 0.258806 -3.781264 0.073045
H14 -1.051665 -2.642476 0.098651
O15 0.801095 1.660096 0.065248
H16 5.831832 0.324500 -0.226280
C17 -3.353572 -1.060506 -0.141960
N18 -2.445227 0.007517 0.021603
C19 -2.811792 1.310746 0.108540
C20 -5.039207 0.509132 -0.137731
N21 -4.688732 -0.766981 -0.221510
H22 -6.110683 0.701787 -0.206172
O23 -2.898015 -2.205385 -0.205169
N24 -1.848512 2.227644 0.283096
H25 -0.832061 1.984125 0.214579
H26 -2.112521 3.197894 0.258093
C27 -4.184136 1.594958 0.024090
H28 -4.548649 2.611178 0.086268
O29 2.767841 3.749074 -0.119445
H30 3.434890 3.045505 -0.137983
H31 1.961850 3.203999 -0.054283

9HG·[C – H]⁻_PT·W39

C1 0.880772 -1.274200 -0.050714
C2 2.319608 -1.287239 0.025541
H3 -1.530736 0.068542 -0.089585
C4 1.062501 1.094262 -0.195415
H5 5.034950 0.366058 0.100638
C6 4.408470 -1.716627 0.176100
N7 0.311421 -0.021514 -0.161201
N8 3.247301 -2.314913 0.141195
N9 4.307466 -0.337764 0.090088
N10 2.408578 1.164302 -0.110510
C11 2.965610 -0.056207 -0.006539
N12 0.398411 2.279546 -0.362663
H13 0.931263 3.113443 -0.180821
H14 -0.606343 2.313540 -0.182700
O15 0.160883 -2.302208 -0.019280
H16 5.366828 -2.208318 0.260975
C17 -3.207894 1.328216 0.110360
N18 -2.578828 0.072712 -0.023987
C19 -3.242546 -1.110002 -0.065059
C20 -5.215934 0.201570 0.167137
N21 -4.573525 1.361205 0.206558
H22 -6.301779 0.269438 0.247445
O23 -2.495098 2.335637 0.134967
N24 -2.523952 -2.232112 -0.214251
H25 -1.471729 -2.234042 -0.154678
H26 -3.011948 -3.109595 -0.152861
C27 -4.642857 -1.059518 0.037574
H28 -5.237439 -1.962552 0.011021
O29 4.750508 2.638950 0.037053
H30 4.733580 3.169998 0.838059
H31 3.818527 2.312684 -0.069928

9HG·[C – H]⁻_PT·W1′2′

C1 -1.849849 -0.879460 0.012545
C2 -3.230723 -0.486698 -0.074926
H3 0.812017 -0.264418 0.102094
C4 -1.374355 1.438577 0.228671
H5 -5.405233 1.830106 -0.107204
C6 -5.354372 -0.322489 -0.254167
N7 -0.954755 0.156686 0.162575
N8 -4.403452 -1.215420 -0.230388
N9 -4.875874 0.973645 -0.122630
N10 -2.640279 1.888208 0.143133
C11 -3.505108 0.878512 -0.005068
N12 -0.407738 2.389300 0.437802
H13 -0.696959 3.336732 0.258383
H14 0.564142 2.151956 0.245403
O15 -1.450124 -2.072206 -0.042931
H16 -6.409908 -0.527096 -0.362658
C17 2.791673 0.448303 -0.040819
N18 1.823864 -0.564008 0.054341
C19 2.117373 -1.889641 0.095114
C20 4.397347 -1.214612 -0.056961
N21 4.110880 0.083377 -0.096905
H22 5.458102 -1.458950 -0.104643
O23 2.416872 1.626630 -0.070308
N24 1.105475 -2.755897 0.199212
H25 0.089341 -2.454652 0.119834
H26 1.326360 -3.736762 0.159134
C27 3.478495 -2.248035 0.035733
H28 3.781565 -3.285607 0.063783
O29 5.265429 2.763310 -0.304344
H30 5.154032 1.795188 -0.246862
H31 4.339399 3.033666 -0.257304

7HG·[C – H]⁻·W1′2′

C1 -1.878932 -0.933410 -0.071642
C2 -3.211402 -0.441230 -0.091093
H3 0.050285 -0.150736 0.099111
C4 -1.322534 1.444284 0.188278
C5 -5.376102 -0.104294 -0.165316
N6 -0.970318 0.109505 0.073448
N7 -4.429396 -1.084522 -0.212464
N8 -4.873738 1.104511 -0.024969
N9 -2.572864 1.886318 0.164627
C10 -3.503108 0.917069 0.025006
N11 -0.301782 2.305518 0.349421
H12 -0.551923 3.280073 0.341302
H13 0.693039 2.022492 0.217271
O14 -1.523957 -2.119938 -0.166671
H15 -6.430372 -0.330050 -0.239002
C16 2.736936 0.406007 -0.008019
N17 1.817526 -0.617426 0.111539
C18 2.245800 -1.881342 0.133671
C19 4.473279 -1.111364 -0.091328
N20 4.088853 0.160056 -0.111433
H21 5.546908 -1.283177 -0.176385
O22 2.318695 1.596359 -0.025948
N23 1.303172 -2.866749 0.300772
H24 0.325681 -2.626864 0.130013
H25 1.576878 -3.801425 0.045333
C26 3.617447 -2.194706 0.027426
H27 3.978089 -3.215532 0.050736
H28 -4.565751 -2.077320 -0.313568
O29 4.871912 2.976429 -0.296083
H30 3.904243 2.958984 -0.217811
H31 5.021230 2.014181 -0.265873

7HG·[C – H]⁻·W67

C1 1.293935 0.520894 -0.038920
C2 2.643122 0.095532 -0.040432
H3 -0.616850 -0.318557 0.065953
C4 0.816341 -1.871007 0.120809
C5 4.811429 -0.158226 -0.082288
N6 0.418343 -0.543510 0.047219
N7 3.838800 0.788901 -0.112449
N8 4.355401 -1.395039 -0.001716
N9 2.084073 -2.263850 0.106383
C10 2.981558 -1.259953 0.026750
N11 -0.174445 -2.770903 0.228592
H12 0.115584 -3.733910 0.192850
H13 -1.184161 -2.519355 0.079138
O14 0.876761 1.705647 -0.104172
H15 5.858636 0.106039 -0.122605
C16 -3.252728 -1.012494 -0.116503
N17 -2.388278 0.056863 0.081012
C18 -2.886770 1.291188 0.161761
C19 -5.059124 0.413689 -0.163209
N20 -4.612832 -0.831024 -0.243011
H21 -6.139162 0.536968 -0.267506
O22 -2.768678 -2.170237 -0.184704
N23 -1.998674 2.319805 0.410852
H24 -1.016306 2.130399 0.217012
H25 -2.312524 3.240641 0.147688
C26 -4.267005 1.538117 0.038857
H27 -4.683382 2.535493 0.110909
H28 3.918157 1.804448 -0.145231
O29 2.898683 3.500437 -0.175465
H30 2.075335 2.946609 -0.182460
H31 2.789277 4.109312 0.559858

7HG·[C – H]⁻·W39

C1 -0.887611 -1.327441 -0.061889
C2 -2.307502 -1.232723 -0.078062
H3 0.752402 -0.029203 0.054375
C4 -1.016291 1.121990 0.090780
C5 -4.481570 -1.523690 -0.127050
N6 -0.308073 -0.066411 0.025147
N7 -3.298095 -2.195201 -0.152443
N8 -4.334647 -0.216173 -0.042829
N9 -2.347305 1.188988 0.073091
C10 -2.965411 -0.009869 -0.010058
N11 -0.281239 2.236555 0.189985
H12 -0.793118 3.102744 0.165239
H13 0.766808 2.236917 0.061423
O14 -0.219093 -2.370352 -0.115198
H15 -5.430984 -2.036692 -0.173136
C16 3.122706 1.277423 -0.110225
N17 2.544172 0.030542 0.081385
C18 3.326704 -1.047212 0.163850
C19 5.221009 0.335311 -0.150042
N20 4.485026 1.434505 -0.230664
H21 6.298847 0.479391 -0.249105
O22 2.369801 2.283157 -0.178450
N23 2.715204 -2.259376 0.407378
H24 1.715519 -2.322777 0.217206
H25 3.248951 -3.079373 0.167181
C26 4.726263 -0.948580 0.046430
H27 5.373448 -1.814156 0.118933
H28 -3.150560 -3.189947 -0.211418
O29 -4.931933 2.745010 0.120768
H30 -3.968485 2.623245 0.132571
H31 -5.218124 1.822066 0.060013

7HG·[C – H]⁻·W23

C1 -1.012879 -1.394712 -0.058881
C2 -2.432401 -1.297336 -0.065616

H3 0.633758 -0.104764 0.049752
C4 -1.129543 1.055169 0.090230
C5 -4.605757 -1.583897 -0.111259
N6 -0.426873 -0.135808 0.021734
N7 -3.422857 -2.259828 -0.138015
N8 -4.459714 -0.276651 -0.028759
N9 -2.464569 1.119158 0.082509
C10 -3.092921 -0.075349 0.002879
N11 -0.401240 2.172083 0.174503
H12 -0.914075 3.042341 0.180752
H13 0.644998 2.165997 0.063337
O14 -0.348300 -2.440195 -0.115765
H15 -5.555466 -2.097282 -0.155023
C16 3.014445 1.176094 -0.109830
N17 2.428058 -0.068216 0.080003
C18 3.203147 -1.151243 0.157562
C19 5.106402 0.218097 -0.160084
N20 4.378599 1.322705 -0.235714
H21 6.185081 0.354261 -0.262892
O22 2.269078 2.186237 -0.171404
N23 2.583618 -2.359969 0.400839
H24 1.582847 -2.413628 0.212859
H25 3.109588 -3.182571 0.152293
C26 4.603107 -1.062860 0.035667
H27 5.244273 -1.933222 0.105028
H28 -3.275420 -3.254627 -0.194862
O29 -3.208293 3.834814 0.177937
H30 -3.125519 2.851867 0.189121
H31 -3.656709 4.026677 -0.650216

7HG·[C – H]$^{-}$_PT·W67
C1 1.261749 0.447697 0.064405
C2 2.634546 0.104233 -0.033901
H3 -1.423380 -0.250745 0.099463
C4 0.895007 -1.871879 0.189656
C5 4.807780 -0.060654 -0.240792
N6 0.408445 -0.597383 0.175471
N7 3.796251 0.846788 -0.172216
N8 4.408291 -1.316059 -0.163989
N9 2.167575 -2.261398 0.079954
C10 3.031969 -1.234437 -0.032340
N11 -0.041685 -2.861282 0.372115
H12 0.286051 -3.788171 0.153603
H13 -1.018347 -2.656551 0.167298
O14 0.833377 1.661191 0.048345
H15 5.838036 0.248955 -0.348480
C16 -3.352967 -1.066963 -0.129955
N17 -2.438709 -0.000147 0.028827
C18 -2.798991 1.305237 0.082070
C19 -5.028332 0.515273 -0.178054
N20 -4.686472 -0.762987 -0.231197
H21 -6.097413 0.714781 -0.263804
O22 -2.905950 -2.213294 -0.169655
N23 -1.832327 2.223803 0.254634
H24 -0.818778 1.977909 0.186461
H25 -2.093987 3.191792 0.174982
C26 -4.165959 1.598820 -0.027982
H27 -4.523468 2.618814 0.009199
H28 3.835475 1.863757 -0.183819
O29 2.724982 3.534693 -0.043010
H30 1.955681 2.894491 -0.039098
H31 2.662455 4.000948 0.794929

7HG·[C – H]$^{-}$_PT·W39
C1 -0.861628 -1.222814 0.046523
C2 -2.285158 -1.211633 -0.032672
H3 1.551226 0.092297 0.083325
C4 -1.074178 1.129505 0.158369
C5 -4.445406 -1.591233 -0.190025
N6 -0.296788 0.013782 0.141168
N7 -3.233835 -2.213867 -0.143186
N8 -4.356226 -0.277753 -0.119396
N9 -2.411989 1.194240 0.075586
C10 -2.995882 -0.018691 -0.019483
N11 -0.406550 2.315664 0.307144
H12 -0.943039 3.143802 0.108384
H13 0.595762 2.346383 0.123791
O14 -0.179551 -2.289550 0.027191
H15 -5.369730 -2.144038 -0.276086
C16 3.235214 1.336754 -0.127805
N17 2.598179 0.085263 0.026170
C18 3.254872 -1.098784 0.094006
C19 5.237195 0.196391 -0.147295
N20 4.603171 1.357758 -0.213483
H21 6.324089 0.255462 -0.220107
O22 2.528615 2.344800 -0.177510
N23 2.529759 -2.217689 0.260653
H24 1.483625 -2.220652 0.184961
H25 3.016022 -3.096793 0.211709
C26 4.654599 -1.059844 0.001311
H27 5.243585 -1.965628 0.049714
H28 -3.041340 -3.201478 -0.181692
O29 -4.981447 2.685049 0.009703
H30 -4.019572 2.541742 0.065990
H31 -5.279390 1.766809 -0.065245

7HG·[C – H]$^{-}$_PT·W1′2′
C1 1.846142 0.829274 0.011708
C2 3.202698 0.411120 -0.074080
H3 -0.808410 0.248160 0.110230
C4 1.390928 -1.475394 0.246908
C5 5.375869 0.154178 -0.265891

N6 0.953284 -0.186892 0.173118
N7 4.391258 1.100240 -0.242329
N8 4.925691 -1.075096 -0.127892
N9 2.646971 -1.922820 0.158065
C10 3.549859 -0.935367 -0.004490
N11 0.415857 -2.418936 0.473620
H12 0.704907 -3.367151 0.295726
H13 -0.549593 -2.181331 0.257661
O14 1.493343 2.048024 -0.058981
H15 6.416452 0.421081 -0.387037
C16 -2.793545 -0.443144 -0.044733
N17 -1.815530 0.560773 0.060637
C18 -2.096478 1.887617 0.109482
C19 -4.382557 1.237603 -0.050906
N20 -4.109565 -0.061662 -0.100079
H21 -5.440578 1.493657 -0.098379
O22 -2.431346 -1.622721 -0.083415
N23 -1.076254 2.746944 0.222016
H24 -0.066518 2.444141 0.128721
H25 -1.291633 3.728920 0.181589
C26 -3.452219 2.261393 0.050662
H27 -3.744550 3.301843 0.085492
H28 4.483976 2.098847 -0.330520
O29 -5.344186 -2.697839 -0.341187
H30 -5.173461 -1.738713 -0.269666
H31 -4.439258 -3.030714 -0.297217

7HG·[C – H]$^{-}$_PT·W23
C1 0.969802 -1.297541 -0.035291
C2 2.394453 -1.290948 0.019641
H3 -1.448299 0.016500 -0.076614
C4 1.181690 1.053769 -0.155743
C5 4.553203 -1.678264 0.155917
N6 0.403618 -0.061454 -0.123079
N7 3.338060 -2.298243 0.124350
N8 4.471579 -0.364900 0.081181
N9 2.525255 1.108714 -0.097636
C10 3.114088 -0.102980 -0.006516
N11 0.523824 2.241301 -0.283135
H12 1.067240 3.081354 -0.153275
H13 -0.483105 2.277758 -0.137669
O14 0.286876 -2.363954 -0.001227
H15 5.475522 -2.236273 0.234011
C16 -3.137375 1.260258 0.095438
N17 -2.495540 0.007090 -0.026186
C18 -3.148342 -1.180264 -0.069138
C19 -5.135924 0.113488 0.136021
N20 -4.506276 1.278160 0.176718
H21 -6.223331 0.170335 0.204265
O22 -2.434871 2.271217 0.122676
N23 -2.419821 -2.300546 -0.207375
H24 -1.372506 -2.299011 -0.138883
H25 -2.904120 -3.179720 -0.143564
C26 -4.548631 -1.143915 0.018401
H27 -5.134402 -2.052623 -0.011415
H28 3.140096 -3.284495 0.167602
O29 3.440918 3.747536 -0.011664
H30 3.255193 2.776703 -0.094524
H31 3.941653 3.818609 0.805559

Cartesian coordinates for the structures in Fig. S3, optimized at B3LYP/6-311++G(d,p).

9HG·[C – H]$^-$
Precursor_C (open shell)
O1 -4.334090 -1.323580 1.003972
O2 -5.469861 -1.999175 0.825144
C3 1.848230 -0.979364 -0.160061
C4 3.276960 -0.931772 -0.027970
H5 0.240994 0.357855 -0.153290
C6 1.978527 1.479263 0.106572
C7 5.367218 -1.324168 0.121499
N8 1.283604 0.308560 -0.076221
N9 4.229585 -1.937469 -0.047417
N10 5.219219 0.049221 0.253282
N11 3.302867 1.529306 0.233370
C12 3.874044 0.315582 0.158399
N13 1.257631 2.611810 0.145429
H14 1.766991 3.459586 0.326800
H15 0.219798 2.622725 0.108680
O16 1.126701 -1.963466 -0.326949
H17 6.338340 -1.795255 0.160667
C18 -2.222308 1.690145 -0.117233
N19 -1.611216 0.448611 -0.266758
C20 -2.357982 -0.620933 -0.451052
C21 -4.331542 0.780130 -0.344820
N22 -3.603851 1.846221 -0.141984
H23 -5.412142 0.909604 -0.367362
O24 -1.499864 2.690877 0.047307
N25 -1.776426 -1.823712 -0.632045
H26 -0.764500 -1.921209 -0.510184
H27 -2.355096 -2.640076 -0.512648
C28 -3.822867 -0.565733 -0.451391
H29 -4.329317 -1.256044 -1.118827
H30 5.940270 0.738824 0.393112

TS (open shell)
O1 -4.334090 -1.323580 1.003972
O2 -5.469861 -1.999175 0.825144
C3 1.848230 -0.979364 -0.160061
C4 3.276960 -0.931772 -0.027970
H5 0.240994 0.357855 -0.153290
C6 1.978527 1.479263 0.106572
C7 5.367218 -1.324168 0.121499
N8 1.283604 0.308560 -0.076221
N9 4.229585 -1.937469 -0.047417
N10 5.219219 0.049221 0.253282
N11 3.302867 1.529306 0.233370
C12 3.874044 0.315582 0.158399
N13 1.257631 2.611810 0.145429
H14 1.766991 3.459586 0.326800
H15 0.219798 2.622725 0.108680
O16 1.126701 -1.963466 -0.326949
H17 6.338340 -1.795255 0.160667
C18 -2.222308 1.690145 -0.117233
N19 -1.611216 0.448611 -0.266758
C20 -2.357982 -0.620933 -0.451052
C21 -4.331542 0.780130 -0.344820
N22 -3.603851 1.846221 -0.141984
H23 -5.412142 0.909604 -0.367362
O24 -1.499864 2.690877 0.047307
N25 -1.776426 -1.823712 -0.632045
H26 -0.764500 -1.921209 -0.510184
H27 -2.355096 -2.640076 -0.512648
C28 -3.822867 -0.565733 -0.451391
H29 -4.329317 -1.256044 -1.118827
H30 5.940270 0.738824 0.393112

9HG·[5′-OOC – H]$^-$
O1 4.470248 -1.632308 -0.185413
O2 5.767054 -1.626808 0.514016
C3 -1.862168 -0.987763 -0.104356
C4 -3.296432 -0.938971 -0.071688
H5 -0.263476 0.353768 -0.019804
C6 -2.011174 1.470164 0.160598
C7 -5.392096 -1.328267 -0.073224
N8 -1.307292 0.302490 0.015109
N9 -4.246101 -1.943153 -0.159091
N10 -5.252503 0.044697 0.068475
N11 -3.338366 1.523456 0.191248
C12 -3.904399 0.309239 0.071206
N13 -1.291492 2.602018 0.289199
H14 -1.810553 3.462222 0.328220
H15 -0.266484 2.627095 0.196116
O16 -1.126400 -1.968667 -0.216934
H17 -6.364036 -1.798108 -0.104653
C18 2.188353 1.677924 -0.172680
N19 1.560662 0.443716 -0.076347
C20 2.311557 -0.629802 0.057980
C21 4.289383 0.749623 -0.319896
N22 3.552123 1.775218 -0.550304
H23 5.334990 0.740278 -0.619353
O24 1.533678 2.709783 -0.022235
N25 1.791904 -1.849636 0.053052
H26 0.787661 -1.994187 -0.085543
H27 2.449724 -2.616935 0.088886
C28 3.797860 -0.519899 0.305498
H29 3.949036 -0.470138 1.404611
H30 -5.981363 0.734871 0.156014

9HG·[C – H]⁻_PT
Precursor_C_PT (open shell)
O1 -4.617505 -3.328289 0.293933
O2 -5.086165 -4.159713 -0.470138
C3 1.541887 -0.878444 0.022076
C4 2.950768 -1.196959 0.049326
C5 2.228082 1.388674 -0.154308
C6 4.898915 -2.069922 0.132816
N7 1.252026 0.464242 -0.082962
N8 3.633289 -2.397327 0.145415
N9 5.097748 -0.701952 0.033743
N10 3.566703 1.175146 -0.121792
C11 3.845549 -0.123962 -0.021594
N12 1.837431 2.686309 -0.298163
H13 2.554373 3.382965 -0.189029
H14 0.860054 2.948859 -0.154164
O15 0.627470 -1.732245 0.091071
H16 5.728234 -2.760065 0.191120
C17 -1.890668 2.556240 0.072874
N18 -1.557495 1.186788 0.020317
C19 -2.469506 0.180971 0.011476
C20 -4.100391 1.911265 0.112346
N21 -3.213589 2.899390 0.119867
H22 -5.144272 2.225135 0.151548
O23 -0.968198 3.378655 0.073530
N24 -2.023287 -1.080521 -0.053422
H25 -1.004987 -1.313486 -0.006403
H26 -2.699156 -1.825489 -0.005342
C27 -3.824528 0.549642 0.061711
H28 -4.604549 -0.198755 0.061751
H29 5.972869 -0.204721 0.001977
H30 -0.537821 0.948733 -0.019984

TS_PT (open shell)
O1 -4.239120 -1.374895 0.957949
O2 -5.304525 -2.143473 0.730082
C3 1.755308 -0.857741 -0.177267
C4 3.181611 -0.924008 -0.032593
H5 -0.560162 0.524083 -0.134059
C6 2.002884 1.495042 0.031343
C7 5.244616 -1.444273 0.156858
N8 1.215799 0.406993 -0.129985
N9 4.073270 -1.989007 -0.022183
N10 5.182687 -0.062087 0.268391
N11 3.337721 1.517136 0.188576
C12 3.854350 0.284122 0.146030
N13 1.377136 2.713657 -0.000171
H14 1.924659 3.489642 0.332512
H15 0.368109 2.758954 0.117218
O16 1.016841 -1.869120 -0.336302
H17 6.184110 -1.974524 0.218163
C18 -2.282986 1.764541 -0.013690
N19 -1.623260 0.520020 -0.166268
C20 -2.255675 -0.636163 -0.409939
C21 -4.299161 0.695313 -0.377656
N22 -3.652272 1.806425 -0.122452
H23 -5.380852 0.763076 -0.467442
O24 -1.593962 2.756731 0.207301
N25 -1.572026 -1.748507 -0.576344
H26 -0.492804 -1.782073 -0.481078
H27 -2.102028 -2.604608 -0.642622
C28 -3.723064 -0.631218 -0.447737
H29 -4.160112 -1.336639 -1.149569
H30 5.944520 0.582056 0.405598

9HG·[5′-OOC – H]⁻_PT
O1 4.315868 -1.705674 -0.188682
O2 5.631951 -1.706754 0.462423
C3 -1.743964 -0.872529 -0.021419
C4 -3.175620 -0.935455 -0.082692
H5 0.469220 0.521616 0.045530
C6 -2.023232 1.473014 0.262507
C7 -5.242605 -1.449694 -0.229523
N8 -1.219791 0.391144 0.147638
N9 -4.058122 -1.994599 -0.247887
N10 -5.198295 -0.073049 -0.059614
N11 -3.363071 1.496845 0.209519
C12 -3.867649 0.268907 0.037072
N13 -1.402753 2.677054 0.492312
H14 -1.981461 3.487674 0.344672
H15 -0.416621 2.768591 0.271295
O16 -0.988102 -1.877581 -0.113201
H17 -6.180467 -1.976230 -0.332181
C18 2.202977 1.750849 -0.239619
N19 1.547128 0.522423 -0.010094
C20 2.214576 -0.633741 0.121268
C21 4.227896 0.662677 -0.406483
N22 3.543589 1.724493 -0.649887
H23 5.255773 0.579447 -0.750399
O24 1.568267 2.785654 -0.158674
N25 1.602032 -1.779716 0.165968
H26 0.527176 -1.846384 0.057524
H27 2.209077 -2.588794 0.231911
C28 3.707776 -0.556729 0.293193
H29 3.910150 -0.475869 1.383157
H30 -5.972675 0.568831 -0.007935