

Indolyne Experimental and Computational Studies: Synthetic Applications and Origins of Selectivities of Nucleophilic Additions

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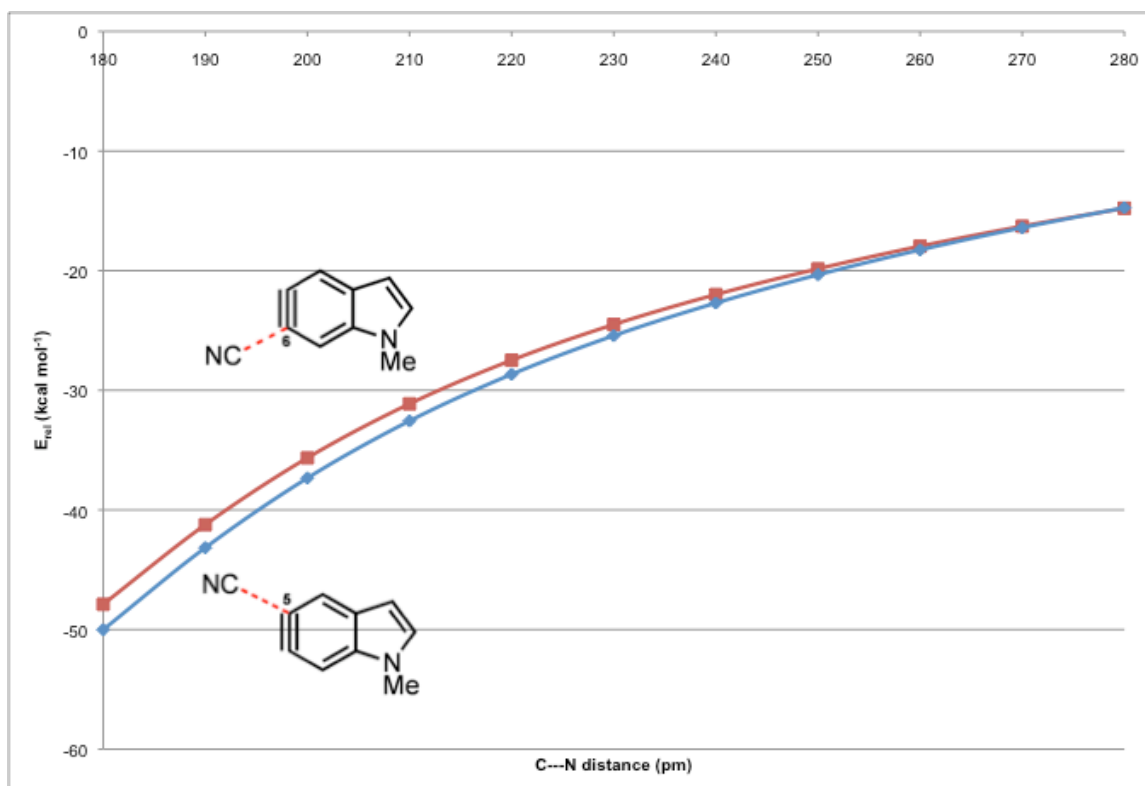
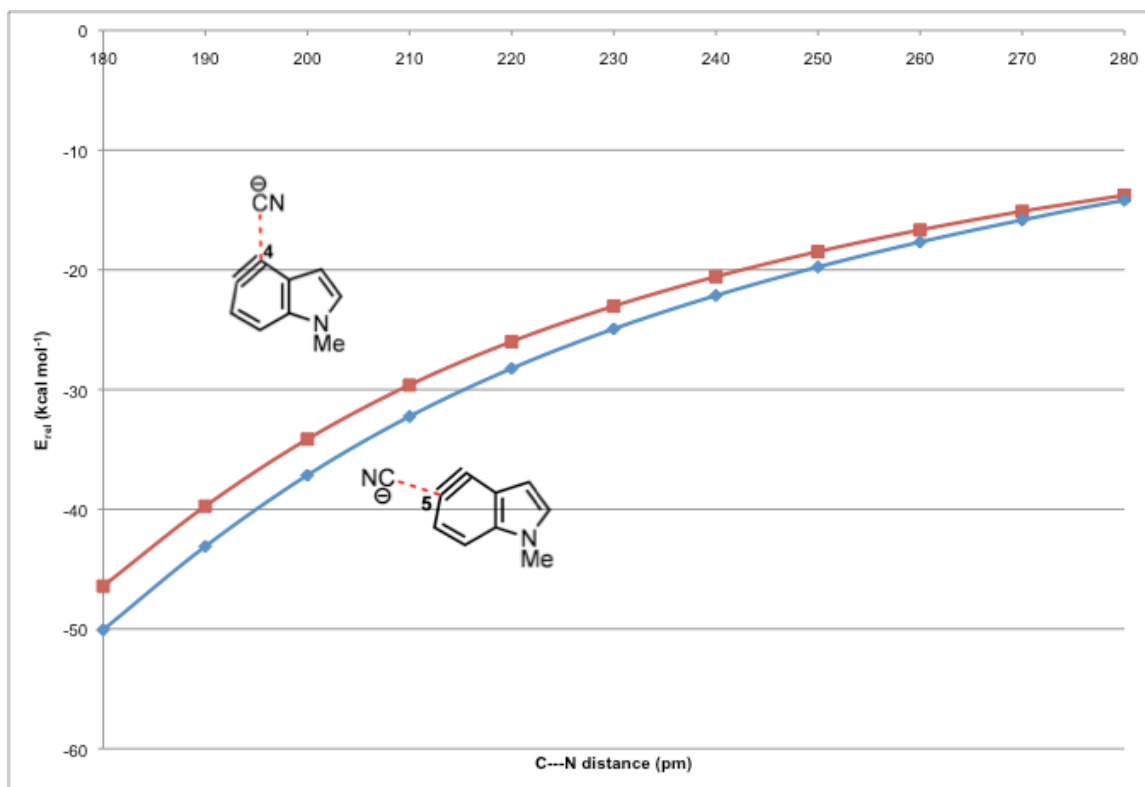
SUPPORTING INFORMATION

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Full reference 35:

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S.

Figure S1. B3LYP/6-31G(d) energy scan along the N---C coordinate for cyanide attack of 4,5-indolyne, 5,6-indolyne and 6,7-indolyne



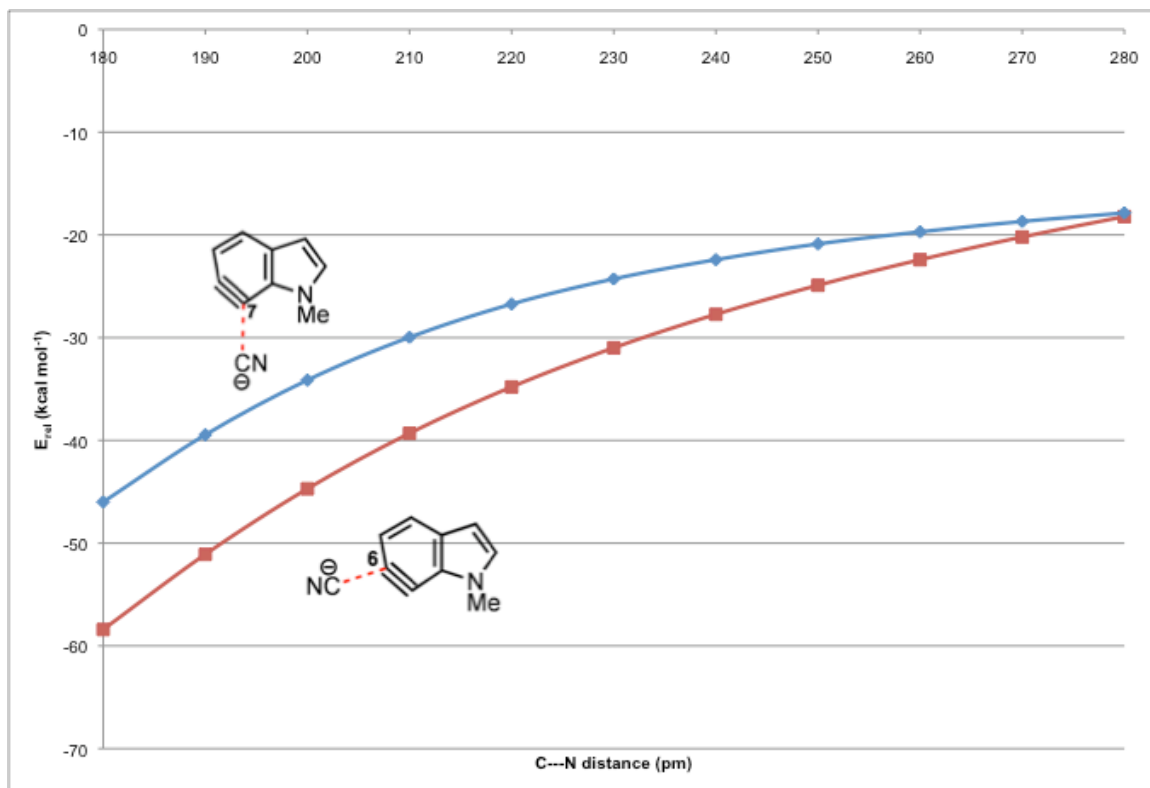


Figure S2. B3LYP/6-31G(d) energy scan along the N---C coordinate for aniline attack of 6,7-indolyne

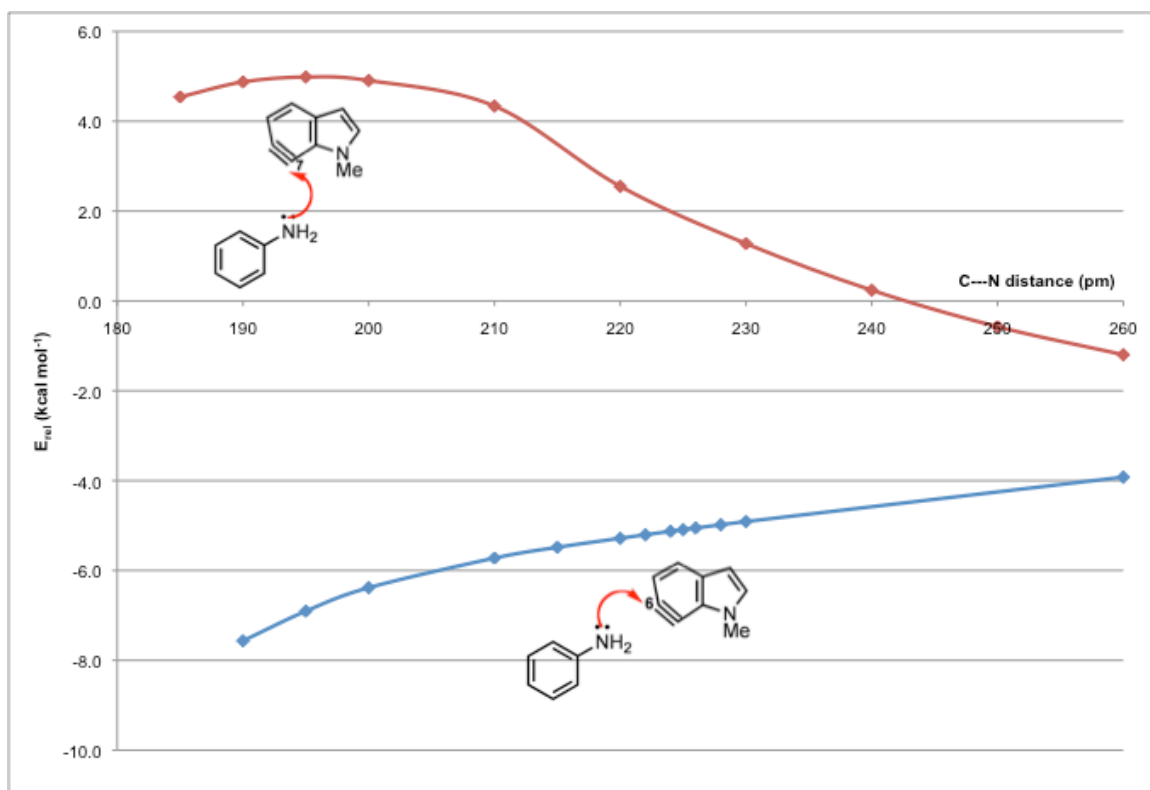
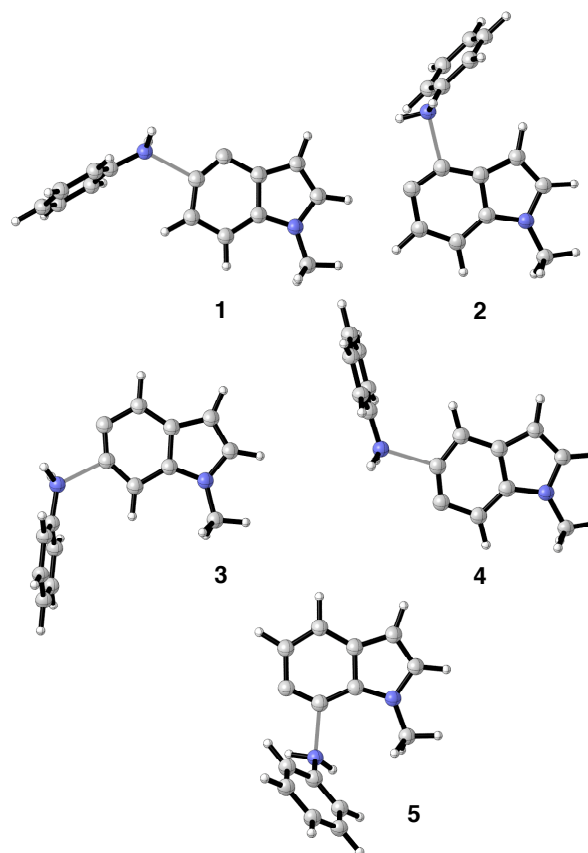


Figure S3. Comparison of B3LYP/6-31G(d) computed activation barriers and distortion energies with MP2, B2PLYP and M06-2X and with larger basis sets.



		6-31G(d)			6-311+G(d,p)	
		B3LYP	MP2	B2PLYP	M06-2X	B3LYP
1	$\Delta\Delta E$	2.7	3.0	2.3	1.9	2.7
	ΔE_d	3.5	3.9	4.0	4.4	3.9
2	ΔE_i	5.8	4.6	5.3	8.0	4.4
	ΔE_d	4.9	6.7	6.0	6.1	5.6
3	ΔE_i	5.2	4.4	5.0	7.8	3.4
	$\Delta\Delta E$	1.7	1.3	1.5	0.7	1.6
4	ΔE_d	5.8	7.8	7.0	7.1	6.5
	ΔE_i	6.6	6.4	6.7	10.2	5.6
5	ΔE_d	3.4	4.5	4.1	4.4	3.9
	ΔE_i	5.9	4.3	5.3	8.2	4.6
5	ΔE_d	8.8	12.8	10.7	10.4	9.4
	ΔE_i	3.8	4.3	4.2	7.7	0.9

The B3LYP/6-31G(d) transition structures for aniline addition to 4,5-, 5,6-, and 6,7-indolyne were used to investigate the effects of level of theory and basis set size on the relative energies and distortion energies of the regioisomeric pathways. Single point energy calculations were used to compute relative energies and distortion energies. Reassuringly, the regiochemical preference computed at each level of theory and basis set size is the same, and the computed distortion energies are always in accord – i.e. the favored transition structure has a lower distortion energy than the disfavored structure for all methods. The unfavored TS for 6,7-indolyne has the highest distortion energy of all regioisomeric pathways at all levels. We can be confident about the computations, and these results demonstrate the predictive power of the distortion model for explaining the observed regioselectivity.

B3LYP/6-31G(d) cartesian coordinates, electronic energies, enthalpies and free energies at 298 K.

29:

C	0.015323	-0.275344	-0.000006	C	-2.295377	-1.071152	0.000247
C	-0.35041	1.122809	0.000058	C	-0.915782	-1.336535	0.00009
C	-1.739268	1.250927	0.000252	C	1.885554	0.971536	-0.00059
C	-2.547665	0.301692	0.000313	C	0.856562	1.881399	0.000049
				H	2.954264	1.139411	-0.000943
				H	0.956913	2.957192	0.000201
				N	1.39782	-0.321235	-0.000155
				C	2.200655	-1.527823	-0.000112
				H	1.997626	-2.133443	0.890803

H 1.997245 -2.133715 -0.890753
H 3.257322 -1.251701 -0.000383
H -0.572692 -2.367875 0.000038
H -3.032969 -1.866275 0.000323

E(B3LYP/6-31G(d)): -401.790665387
H(B3LYP/6-31G(d)): -401.648655
G(B3LYP/6-31G(d)): -401.690256

29 - aniline TS (5 attack):

C -2.473848 -1.051074 -0.006821
C -2.625681 0.377607 -0.007621
C -1.533706 1.267591 -0.057754
C -0.24017 0.732028 -0.108111
C -0.263451 -0.654518 -0.100586
C -1.156848 -1.575752 -0.058034
C -4.67106 -0.543946 0.083672
H -1.677988 2.344579 -0.057586
H 0.647508 1.354406 -0.14712
H -5.752372 -0.533399 0.129473
C 2.875976 -0.662588 -0.071876
C 3.406927 -0.36891 1.191888
C 3.468525 -0.111939 -1.216836
C 4.524546 0.455658 1.302392
H 2.941749 -0.786413 2.081604
C 4.585778 0.712058 -1.094652
H 3.052466 -0.331253 -2.19736
C 5.120937 1.000104 0.162693
H 4.931265 0.672011 2.286519
H 5.040564 1.128691 -1.989279
N 1.700116 -1.441996 -0.184508
H 5.992802 1.641125 0.253464
H 1.545188 -2.100087 0.572751
H 1.590264 -1.921475 -1.072523
C -3.797757 -1.600376 0.05192
H -4.063822 -2.648299 0.069093
N -3.978631 0.65621 0.049021
C -4.569762 1.976125 0.06466
H -4.217121 2.556518 0.926331
H -4.327296 2.531451 -0.85025
H -5.65603 1.88024 0.133691

E(B3LYP/6-31G(d)): -689.396053571
H(B3LYP/6-31G(d)): -689.128298
G(B3LYP/6-31G(d)): -689.188532

29 - aniline TS (4 attack):

C 1.10676 -0.036412 -0.294709
C 2.487975 0.009643 0.09025
C 3.170117 1.214933 0.347471
C 2.479503 2.423016 0.226312
C 1.107647 2.423935 -0.155657
C 0.603514 1.254804 -0.364589
C 1.892987 -2.13973 -0.196614
H 4.218755 1.203411 0.637585
H 3.015921 3.350167 0.430653
H 2.047801 -3.210417 -0.210276
C -2.368852 0.585934 -0.407245
C -2.903531 -0.502196 -1.10673
C -2.813262 0.867326 0.890785
C -3.880215 -1.300052 -0.511056
H -2.558677 -0.719521 -2.115388
C -3.792505 0.067109 1.474634
H -2.38254 1.702356 1.436724
C -4.330956 -1.019045 0.779682
H -4.293196 -2.139777 -1.063295
H -4.134822 0.293438 2.480669
N -1.323639 1.367651 -0.976243
H -5.09449 -1.639165 1.239955
H -1.261725 1.285167 -1.988381
H -1.33863 2.352883 -0.720761
C 0.759364 -1.413676 -0.468805
H -0.204462 -1.818531 -0.740802
N 2.936944 -1.300284 0.138892
C 4.280581 -1.711096 0.486686
H 5.014477 -1.28836 -0.210023
H 4.540161 -1.389369 1.502442
H 4.343521 -2.800816 0.43986

E(B3LYP/6-31G(d)): -689.392871797
H(B3LYP/6-31G(d)): -689.124766
G(B3LYP/6-31G(d)): -689.184187

29 - p-cresol TS (5 attack):

C -2.440508 -0.957585 -0.188849
C -2.846822 0.399553 0.039055
C -2.016946 1.503903 -0.22977
C -0.74463 1.247604 -0.742779
C -0.48037 -0.108322 -0.909174
C -1.147638 -1.252879 -0.702464
C -4.547142 -0.938344 0.636108
H -2.344998 2.524194 -0.053853
H -0.048134 2.044295 -0.982518
H -5.537959 -1.160859 1.010696
H 0.608227 -1.51058 -1.476804

O 0.965491 -0.552447 -1.546369
C 2.139263 -0.34238 -0.764963
C 2.289773 -0.968696 0.469243
C 3.100657 0.510913 -1.28245
C 3.45574 -0.729472 1.191477
H 1.503895 -1.612943 0.849931
C 4.258272 0.743652 -0.535318
H 2.946559 0.974802 -2.251325
C 4.456208 0.128669 0.70595
H 3.588784 -1.215291 2.155102
H 5.020031 1.410476 -0.930902
C 5.710493 0.376399 1.511187
H 5.476533 0.820407 2.486518
H 6.251422 -0.557938 1.704532
H 6.392452 1.055353 0.990468
C -4.911256 1.544204 0.911525
H -4.432722 2.100503 1.72769
H -5.039378 2.221915 0.05832
H -5.899722 1.220815 1.246485
N -4.134089 0.382333 0.541036
C -3.553448 -1.776505 0.205125
H -3.600171 -2.856196 0.165945

E(B3LYP/6-31G(d)): -748.561266971
H(B3LYP/6-31G(d)): -748.278796
G(B3LYP/6-31G(d)): -748.341154

29 - p-cresol TS (4 attack):

C 1.458641 -0.141625 -0.455622
C 2.726677 -0.008667 0.191001
C 3.223224 1.228356 0.641219
C 2.448585 2.374198 0.452222
C 1.166889 2.332418 -0.174537
C 0.832781 1.094983 -0.547047
C 2.416136 -2.170657 -0.340741
H 4.195313 1.28731 1.126409
H 2.853166 3.3232 0.805674
H 2.678263 -3.218832 -0.395851
O -0.630076 1.23018 -1.295024
C -1.773628 0.661764 -0.659411
C -2.468176 -0.314127 -1.357353
C -2.154889 1.075133 0.613391
C -3.586983 -0.895949 -0.757072
H -2.138715 -0.605911 -2.349372
C -3.279383 0.487588 1.18856
H -1.571411 1.825298 1.137012
C -4.012943 -0.503556 0.517495
H -4.137937 -1.664149 -1.293646
H -3.588589 0.801234 2.182647

C -5.240518 -1.114616 1.152176
H -5.073926 -1.338031 2.211822
H -6.098076 -0.4314 1.096939
H -5.52855 -2.044583 0.652232
H -0.527163 2.233465 -1.101777
C 1.287798 -1.524529 -0.782376
H 0.442514 -1.98344 -1.274354
N 3.287878 -1.274699 0.245657
C 4.581876 -1.59072 0.812059
H 5.382859 -1.057144 0.286378
H 4.622351 -1.320891 1.874106
H 4.758848 -2.664646 0.718598

E(B3LYP/6-31G(d)): -748.557567242
H(B3LYP/6-31G(d)): -748.274945
G(B3LYP/6-31G(d)): -748.337279

29 - azide TS (4 attack):

C -1.48524 1.762785 0.151168
C -1.632109 0.365651 0.017739
C -0.525247 -0.544518 -0.141667
C 0.676033 0.156633 -0.135643
C 0.827605 1.402957 -0.028243
C -0.206019 2.335856 0.131713
H -2.359427 2.399061 0.264386
H -0.071088 3.409139 0.227968
N 3.50207 1.471625 -0.147506
C -2.431962 -1.728753 -0.149163
H -3.203612 -2.486248 -0.183488
N 3.415456 0.329773 -0.194685
N 2.932171 -0.799456 -0.374207
N -2.783775 -0.401781 0.008153
C -1.068355 -1.861034 -0.243617
C -4.133757 0.106296 0.142648
H -4.270648 0.609495 1.107226
H -4.366096 0.81716 -0.658973
H -4.836016 -0.728165 0.081962
C 3.311227 -1.84149 0.592694
H 2.66811 -2.697465 0.385879
H 4.35551 -2.146838 0.458081
H 3.155533 -1.517213 1.628192
H -0.526772 -2.786357 -0.379291

E(B3LYP/6-31G(d)): -605.884116222
H(B3LYP/6-31G(d)): -605.685085
G(B3LYP/6-31G(d)): -605.741045

29 - azide TS (5 attack):

C 1.038213 -1.64852 -0.169788
C 1.63733 -0.378125 -0.037095
C 0.894237 0.855939 -0.004584
C -0.489719 0.662725 -0.117743
C -0.967141 -0.500375 -0.225405
C -0.357636 -1.749836 -0.276481
H 1.645595 -2.54957 -0.192369
H -0.855465 -2.707808 -0.385508
N -3.367035 -0.320924 -0.347351
C 3.082855 1.327856 0.179007
H 4.060778 1.780369 0.277504
N -3.318457 0.9086 -0.17493
N -2.936496 1.986471 -0.14626
C -4.12102 -1.094509 0.652281
H -3.93215 -2.145319 0.430431
H -3.788394 -0.877298 1.674003
H -5.197938 -0.907354 0.569906
N 2.975405 -0.047908 0.078119
C 1.843291 1.915293 0.132907
C 4.078691 -0.985641 0.084627
H 3.991178 -1.690399 0.920298
H 4.116645 -1.556078 -0.851269
H 5.015012 -0.433477 0.193017
H 1.636212 2.974408 0.190587

E(B3LYP/6-31G(d)): -605.884652343
H(B3LYP/6-31G(d)): -605.685709
G(B3LYP/6-31G(d)): -605.741602

69:

C -0.073079 -0.375868 -0.000013
C 0.593585 0.905225 -0.000001
C 2.013905 0.986048 -0.000163
C 2.544504 -0.284203 -0.000325
C 1.962687 -1.396499 -0.000334
C 0.601587 -1.624414 -0.000185
C -1.639902 1.237959 0.00019
C -0.441972 1.900267 0.000238
H 2.550597 1.929344 -0.000143
H -2.649943 1.627001 0.000279
H -0.309363 2.973263 0.000351
N -1.433978 -0.131354 0.000162
C -2.464416 -1.1481 0.000231
H -2.391359 -1.783963 -0.890484
H -2.391163 -1.784052 0.890867
H -3.442846 -0.662564 0.000364
H 0.090529 -2.582045 -0.000196

E(B3LYP/6-31G(d)): -401.787786989
H(B3LYP/6-31G(d)): -401.645904
G(B3LYP/6-31G(d)): -401.687537

69 - p-cresol TS (5 attack):

C -2.324501 -2.104586 -0.336542
C -3.024918 -0.879953 -0.41291
C -2.432484 0.319023 0.102431
C -1.156084 0.327399 0.693176
C -0.641585 -0.947486 0.666567
C -1.040111 -2.156416 0.235146
H -0.6743 1.209341 1.101937
C 2.003432 -0.641835 0.69149
C 2.413055 -1.109626 -0.554651
C 2.660722 0.39258 1.340608
C 3.524032 -0.518343 -1.150779
H 1.863086 -1.907651 -1.043277
C 3.766337 0.977377 0.718804
H 2.318769 0.721374 2.316727
C 4.216416 0.533723 -0.530052
H 3.856477 -0.879218 -2.121074
H 4.290916 1.786293 1.220901
H -2.801037 -3.002472 -0.734079
O 0.874506 -1.20659 1.341522
H 0.713815 -2.182274 1.08268
C 5.408253 1.172443 -1.204387
H 6.127533 0.418266 -1.544104
H 5.103786 1.748274 -2.087653
H 5.931671 1.855575 -0.528489
C -4.313883 -0.495522 -0.926935
C -4.453769 0.848388 -0.716242
N -3.32275 1.358134 -0.093386
H -5.04334 -1.143726 -1.393369
H -5.274518 1.511859 -0.956376
C -3.103507 2.733859 0.29079
H -2.21998 3.1499 -0.21015
H -3.974478 3.327374 0.003247
H -2.963629 2.826727 1.375518

E(B3LYP/6-31G(d)): -748.555640507
H(B3LYP/6-31G(d)): -748.273247
G(B3LYP/6-31G(d)): -748.335924

69 - p-cresol TS (6 attack):

C 2.368213 -1.543247 0.041682
C 2.901714 -0.240956 0.093243
C 2.188864 0.92294 -0.346439

C 0.88331 0.764146 -0.860026
C 0.513517 -0.555931 -0.835847
C 1.067203 -1.725376 -0.457705
H 0.279064 1.591137 -1.219279
C -2.147322 -0.551268 -0.711129
C -2.436016 -1.094922 0.5378
C -2.943702 0.425927 -1.289376
C -3.568642 -0.643174 1.210453
H -1.776735 -1.839511 0.972592
C -4.068758 0.871068 -0.591728
H -2.688282 0.822627 -2.266708
C -4.402604 0.34371 0.661175
H -3.805104 -1.061264 2.185887
H -4.698857 1.63758 -1.035625
H 2.967223 -2.385767 0.391036
O -1.000485 -0.970853 -1.435525
H -0.726441 -1.927386 -1.216854
C -5.634861 0.807988 1.402016
H -6.420035 0.041076 1.387925
H -5.412361 1.021914 2.453642
H -6.052611 1.715416 0.955152
C 4.217513 1.56175 0.395253
H 5.116897 2.08548 0.692566
N 4.141424 0.18858 0.542842
C 3.054759 2.049042 -0.140978
H 2.841474 3.085789 -0.362654
C 5.177474 -0.669671 1.074699
H 4.831393 -1.197222 1.971921
H 5.490687 -1.415676 0.33426
H 6.043622 -0.059593 1.341892

E(B3LYP/6-31G(d)): -748.559050917
H(B3LYP/6-31G(d)): -748.276447
G(B3LYP/6-31G(d)): -748.339254

69 - aniline TS (5 attack):

C -2.015574 0.283185 -0.015249
C -2.96889 -0.786973 0.040192
C -2.522495 -2.128719 0.034131
C -1.142546 -2.379707 -0.026923
C -0.404312 -1.304059 -0.073852
C -0.626664 0.053071 -0.077875
C -4.068742 1.190837 0.07119
H -3.260788 -2.932032 0.077986
H -4.785363 2.001877 0.096051
C 2.548465 -0.759451 -0.072053
C 3.026166 -0.373077 1.186481
C 3.017783 -0.118014 -1.225039
C 3.979438 0.638657 1.284135

H 2.650459 -0.863901 2.080827
C 3.970885 0.893252 -1.11583
H 2.638127 -0.412768 -2.20038
C 4.456754 1.275873 0.136342
H 4.351101 0.928269 2.263086
H 4.336133 1.381282 -2.015171
N 1.519649 -1.738394 -0.171313
H 5.200945 2.062604 0.217081
H 1.511329 -2.423528 0.580239
H 1.504123 -2.239345 -1.056061
H 0.121708 0.838498 -0.120718
C -4.265494 -0.162449 0.094117
H -5.223349 -0.662529 0.143974
N -2.71241 1.478407 0.00517
C -2.117464 2.794178 -0.034648
H -1.451626 2.955579 0.822986
H -1.537235 2.940766 -0.954911
H -2.9101 3.545519 -0.002703

E(B3LYP/6-31G(d)): -689.390838104
H(B3LYP/6-31G(d)): -689.122821
G(B3LYP/6-31G(d)): -689.182616

69 - aniline TS (6 attack):

C -1.737116 0.765555 -0.00004
C -2.75191 -0.251549 0.000005
C -2.467962 -1.634071 0.000027
C -1.111724 -1.983892 0.000006
C -0.286502 -0.985047 -0.000038
C -0.373319 0.381263 -0.000063
C -3.759652 1.763005 -0.000016
H -3.277005 -2.365936 0.000062
H -4.602904 2.441907 -0.000011
C 2.816697 -0.715121 -0.000013
C 3.335268 -0.238452 1.211765
C 3.335352 -0.238452 -1.211755
C 4.369106 0.695821 1.205954
H 2.926332 -0.599618 2.152368
C 4.369189 0.695822 -1.205874
H 2.926483 -0.599621 -2.152387
C 4.892375 1.167671 0.000058
H 4.767564 1.055058 2.150857
H 4.767712 1.055059 -2.150749
N 1.717377 -1.608282 -0.000049
H 5.698879 1.894871 0.000086
H 1.641391 -2.192395 0.82707
H 1.641418 -2.192356 -0.827198
C -2.4163 2.031005 -0.000053
H -1.963869 3.013277 -0.000084

N -3.97796 0.39664 0.000021
C -5.266651 -0.259794 0.000053
H -5.389322 -0.889961 -0.889441
H -5.389275 -0.889962 0.889551
H -6.053331 0.498529 0.000075
H 0.448903 1.090044 -0.0001

E(B3LYP/6-31G(d)): -689.393611466
H(B3LYP/6-31G(d)): -689.125756
G(B3LYP/6-31G(d)): -689.185633

69 - azide TS (5 attack):

C -1.580244 -0.307081 0.0008
C -1.171808 1.067795 -0.140856
C 0.205201 1.394305 -0.267485
C 0.956358 0.246682 -0.2213
C 0.633935 -0.977138 -0.104855
C -0.679863 -1.399055 0.022856
C -3.42149 0.986136 0.025073
H 0.560084 2.413938 -0.383456
H -4.48423 1.183306 0.083725
H -1.01324 -2.429091 0.123772
C -2.372973 1.854851 -0.119969
N -2.960833 -0.316804 0.099306
C -3.777198 -1.502073 0.251518
H -3.65151 -2.180448 -0.601152
H -3.517758 -2.044424 1.168887
H -4.827181 -1.20606 0.308284
N 3.367547 0.389218 -0.345058
N 3.485322 -0.833138 -0.160032
N 3.263102 -1.954306 -0.120696
C 4.008916 1.269721 0.64501
H 5.101392 1.22341 0.568819
H 3.68538 2.283248 0.406281
H 3.702114 1.026007 1.668788
H -2.446025 2.930459 -0.203347

E(B3LYP/6-31G(d)): -605.88227839
H(B3LYP/6-31G(d)): -605.683404
G(B3LYP/6-31G(d)): -605.739477

69 - azide TS (6 attack):

C 1.431672 0.254965 -0.053841
C 1.488429 -1.177574 0.094476
C 0.296244 -1.948114 0.097722
C -0.825424 -1.155967 -0.052855
C -0.836634 0.107638 -0.172536

C 0.225602 0.983245 -0.202356
C 3.589948 -0.348867 0.136699
H 0.30972 -3.02979 0.201667
H 4.657964 -0.178903 0.183412
H 0.189777 2.062628 -0.317995
C 2.880248 -1.516415 0.211306
N 2.731299 0.727255 -0.021303
C 3.11866 2.115107 -0.149874
H 2.814993 2.523536 -1.121831
H 2.665965 2.725141 0.641497
H 4.205153 2.190454 -0.065892
N -3.456578 -1.587361 -0.145456
N -3.535917 -0.445201 -0.198441
N -3.225497 0.741298 -0.38871
C -3.732765 1.720249 0.585483
H -3.506544 1.427475 1.617395
H -3.22996 2.661697 0.361778
H -4.813685 1.866294 0.47556
H 3.297585 -2.50606 0.336446

E(B3LYP/6-31G(d)): -605.881301368
H(B3LYP/6-31G(d)): -605.68242
G(B3LYP/6-31G(d)): -605.738617

71:

C -0.169112 -0.418218 -0.012586
C 0.509531 0.851133 0.005258
C 1.923551 0.902661 0.012011
C 2.704624 -0.266914 0.007869
C 1.872768 -1.377246 -0.004768
C 0.634664 -1.559191 -0.021088
C -1.727954 1.180817 -0.012652
C -0.527452 1.844093 0.005575
H 2.429529 1.865276 0.026752
H 3.78748 -0.252267 0.020399
H -2.736024 1.573219 -0.01875
H -0.401992 2.918446 0.006271
N -1.524577 -0.189469 -0.032267
C -2.549476 -1.212294 0.03222
H -2.142645 -2.141122 -0.374697
H -2.878047 -1.394189 1.063123
H -3.41312 -0.912126 -0.568259

E(B3LYP/6-31G(d)): -401.792681812
H(B3LYP/6-31G(d)): -401.650794
G(B3LYP/6-31G(d)): -401.693059

71 - aniline TS (7 attack):

C 1.621659 0.225905 0.130251
C 2.866284 -0.229425 -0.415318
C 3.173131 -1.608587 -0.415944
C 2.274812 -2.529717 0.116352
C 1.041995 -2.084311 0.670823
C 0.83008 -0.802038 0.625489
C 2.754758 2.020895 -0.599639
C 3.556008 0.946309 -0.868905
H 4.120701 -1.942357 -0.835882
H 2.5378 -3.587704 0.103164
H 2.911484 3.074682 -0.786988
H 4.527401 0.983156 -1.343459
N 1.573611 1.602078 0.002131
C 0.524006 2.483262 0.461138
H -0.446115 2.187734 0.049031
H 0.457455 2.501308 1.558609
H 0.744335 3.498464 0.122727
C -2.033462 -0.244541 0.619271
C -2.821342 0.909233 0.646178
C -2.331168 -1.284926 -0.269408
C -3.910363 1.025077 -0.220479
H -2.598061 1.706544 1.351858
C -3.421768 -1.158922 -1.126039
H -1.692914 -2.162919 -0.287206
C -4.214668 -0.007256 -1.107169
H -4.523424 1.921583 -0.192026
H -3.652161 -1.966185 -1.815576
N -0.877819 -0.368972 1.466089
H -5.065056 0.081673 -1.776918
H -0.81775 0.378808 2.15729
H -0.834009 -1.272272 1.938221

E(B3LYP/6-31G(d)): -689.386498695
H(B3LYP/6-31G(d)): -689.118223
G(B3LYP/6-31G(d)): -689.175772

71 - azide TS (6 attack):

C 0.776279 -2.267522 -0.147967
C 1.702767 -1.204961 -0.02636
C 1.232679 0.152449 -0.028391
C -0.138996 0.400651 -0.146574
C -0.841679 -0.648301 -0.241831
C -0.598751 -2.013702 -0.268845
H 1.12478 -3.297627 -0.154217
H -1.333318 -2.80325 -0.375414
C 3.129321 -1.129811 0.10749
N -3.168114 -0.061301 -0.329415
N 2.324323 0.985584 0.098518

C 2.271134 2.433398 0.118528
H 1.220766 2.730654 0.085398
H 2.724664 2.830565 1.033786
H 2.78792 2.86229 -0.748144
C 3.460367 0.200545 0.17835
H 3.827466 -1.955258 0.148208
H 4.431304 0.666767 0.2817
N -2.954123 1.155879 -0.220338
N -2.521625 2.21095 -0.244627
C -3.988203 -0.675921 0.730131
H -3.986573 -1.748154 0.533517
H -3.568335 -0.492393 1.725718
H -5.021407 -0.312319 0.693302

E(B3LYP/6-31G(d)): -605.889334006
H(B3LYP/6-31G(d)): -605.69034
G(B3LYP/6-31G(d)): -605.74706

71 - azide TS (7 attack):

C 1.510239 -2.236977 0.161121
C 1.969469 -0.900467 0.090129
C 1.026001 0.174459 -0.048268
C -0.329745 -0.148269 -0.090911
C -0.622355 -1.38024 -0.030598
C 0.141468 -2.534574 0.10344
H 2.224881 -3.05104 0.258106
H -0.238595 -3.548542 0.150459
C 3.265814 -0.284767 0.118076
N -2.812643 0.794587 -0.404729
C -3.305273 1.730723 0.617931
N 1.727474 1.359593 -0.109575
C 1.134944 2.678065 -0.189664
H 1.029289 3.139593 0.800944
H 1.75138 3.32845 -0.817569
H 0.144719 2.58585 -0.642529
C 3.076687 1.06876 -0.002035
H 4.222908 -0.781733 0.203568
H 3.803054 1.870178 -0.028214
H -2.786474 2.674017 0.444888
H -3.089021 1.379297 1.632989
N -3.094082 -0.398356 -0.249814
N -2.946817 -1.540929 -0.219908
H -4.383151 1.899383 0.510213

E(B3LYP/6-31G(d)): -605.885600771
H(B3LYP/6-31G(d)): -605.686636
G(B3LYP/6-31G(d)): -605.742367

71 - p-cresol TS (6 attack):

C 2.592079 -0.186459 0.116265
 C 2.855725 1.092227 -0.474251
 C 1.857373 2.090979 -0.430753
 C 0.640566 1.809785 0.185252
 C 0.548231 0.515328 0.699937
 C 1.384846 -0.548207 0.74443
 C 4.672378 -0.216783 -0.740521
 C 4.183978 1.038731 -1.009433
 H 2.034448 3.071436 -0.86491
 H -0.155561 2.543749 0.255423
 H 5.63594 -0.649015 -0.978207
 H 4.714721 1.826797 -1.527513
 N 3.728142 -0.962235 -0.067364
 C 3.876044 -2.32524 0.397872
 H 2.934018 -2.610107 0.871494
 H 4.082419 -3.008596 -0.434849
 H 4.686499 -2.41035 1.132131
 H -0.237443 -0.84777 1.614838
 O -0.740178 0.056743 1.473419
 C -1.973334 -0.073701 0.752114
 C -2.011551 -0.741806 -0.466523
 C -3.101995 0.482639 1.331826
 C -3.239632 -0.853773 -1.114474
 H -1.101093 -1.152923 -0.889069
 C -4.321125 0.362853 0.660626
 H -3.025202 0.991904 2.286913
 C -4.409782 -0.30276 -0.567922
 H -3.288916 -1.377342 -2.066005
 H -5.21544 0.793883 1.103079
 C -5.725325 -0.408634 -1.303305
 H -5.777802 0.316147 -2.126125
 H -5.860242 -1.403878 -1.740929
 H -6.572765 -0.213308 -0.638935

E(B3LYP/6-31G(d)): -748.569481529
 H(B3LYP/6-31G(d)): -748.287233
 G(B3LYP/6-31G(d)): -748.348541

71 - p-cresol TS (7 attack):

C 1.881798 0.286272 0.126276
 C 3.122202 0.004244 -0.529929
 C 3.572403 -1.330682 -0.640264
 C 2.819977 -2.377029 -0.111859
 C 1.570927 -2.140881 0.534137
 C 1.234425 -0.855872 0.573328
 C 2.770981 2.23843 -0.510792
 C 3.653893 1.279325 -0.925638

H 4.519843 -1.53051 -1.137763
 H 3.205602 -3.392113 -0.205733
 H 2.810726 3.314762 -0.609915
 H 4.585846 1.457235 -1.444982
 N 1.689678 1.651326 0.135113
 C 0.562322 2.362096 0.70365
 H -0.350563 2.215115 0.114797
 H 0.375557 2.026833 1.729004
 H 0.79669 3.428991 0.726587
 O -0.224936 -0.807951 1.417941
 C -1.444286 -0.539533 0.720314
 C -2.413058 0.187414 1.396816
 C -1.643031 -1.002061 -0.577772
 C -3.620393 0.462865 0.749834
 H -2.224678 0.524586 2.411084
 C -2.855402 -0.71799 -1.202323
 H -0.863967 -1.567499 -1.076797
 C -3.861449 0.017017 -0.554757
 H -4.385044 1.032045 1.27225
 H -3.022378 -1.075418 -2.215597
 C -5.166985 0.313474 -1.255184
 H -5.003547 0.878769 -2.180761
 H -5.689348 -0.61068 -1.530979
 H -5.838305 0.899343 -0.620085
 H -0.050632 -1.819662 1.504551

E(B3LYP/6-31G(d)): -748.551658278
 H(B3LYP/6-31G(d)): -748.270214
 G(B3LYP/6-31G(d)): -748.330045

106:

C -0.625572 -1.237592 0.000052
 C 0.625483 -1.237587 0.000053
 C 1.461527 -0.133658 -0.000083
 C 0.703626 1.058433 0.000019
 C -0.703561 1.05847 0.000018
 C -1.461523 -0.133578 -0.000081
 H 2.546764 -0.134878 -0.000033
 H 1.228767 2.011304 0.000098
 H -1.228649 2.01137 0.000104
 H -2.546761 -0.134726 -0.00004

E(B3LYP/6-31G(d)): -230.909947901
 H(B3LYP/6-31G(d)): -230.829175
 G(B3LYP/6-31G(d)): -230.86198

TS-7:

C 3.88705 -0.588729 0.007608
C 3.927839 0.813739 0.057264
C 2.749902 1.580582 0.061136
C 1.490783 0.955304 0.014997
C 1.635804 -0.41107 -0.030146
C 2.631483 -1.235188 -0.03941
H 2.804754 2.665984 0.100107
H 0.555564 1.506551 0.016605
C -1.432141 -0.702039 -0.050956
C -2.028264 -0.426943 1.186699
C -2.028789 -0.236043 -1.229884
C -3.218486 0.296113 1.237984
H -1.559506 -0.779488 2.102277
C -3.218949 0.486303 -1.166999
H -1.560042 -0.44051 -2.189516
C -3.820398 0.755457 0.064383
H -3.677179 0.499485 2.201675
H -3.677823 0.838331 -2.086752
N -0.183918 -1.37593 -0.105047
H -4.748529 1.31739 0.109054
H -0.004534 -2.000382 0.676158
H -0.013015 -1.879304 -0.970954
H 4.888157 1.325544 0.093888
H 4.824578 -1.147001 0.006739

E(B3LYP/6-31G(d)): -518.5154665
H(B3LYP/6-31G(d)): -518.308563
G(B3LYP/6-31G(d)): -518.361094

1,2-naphthalyne:

C 0.143326 0.617574 -0.000072
C -1.027672 1.420643 -0.000047
C -2.284447 0.851643 0.000013
C -2.441029 -0.553032 0.00005
C -1.337982 -1.382475 0.000023
C -0.039244 -0.829142 -0.000003
H -0.921647 2.502757 -0.000015
H -3.165053 1.48808 0.000005
H -3.439674 -0.981219 0.000053
H -1.450715 -2.462257 0.00006
C 2.62434 0.446786 0.000097
C 1.454575 1.198337 0.000019
C 1.21524 -1.465778 -0.000134
C 2.332624 -0.926239 0.000051
H 3.610539 0.898788 -0.000066
H 1.528161 2.283954 -0.000027

E(B3LYP/6-31G(d)): -384.555994196
H(B3LYP/6-31G(d)): -384.425546

G(B3LYP/6-31G(d)): -384.464583

3-methoxybenzyne:

C 0.473899 0.229342 -0.000221
C -0.563984 1.194235 0.000011
C -1.914443 0.825027 0.000161
C -2.340627 -0.527658 0.000144
C -1.214364 -1.312852 -0.000195
C 0.020201 -1.092208 -0.000102
H -2.672148 1.606029 0.000248
H -3.379693 -0.83135 0.000166
H -0.286822 2.244537 0.000029
O 1.758417 0.650704 -0.000299
C 2.747032 -0.37417 0.000301
H 2.65655 -1.00564 -0.891831
H 3.712032 0.13518 0.000088
H 2.656461 -1.004686 0.893095

E(B3LYP/6-31G(d)): -345.438798323
H(B3LYP/6-31G(d)): -345.322633
G(B3LYP/6-31G(d)): -345.362073

1,2-Benzynocyclobutene:

C -0.951521 1.236972 0.000095
C 0.30798 0.636209 0.000013
C 0.50855 -0.757759 -0.000024
C -0.666675 -1.486922 -0.000073
C -1.793665 -0.93086 -0.000068
C -2.113131 0.41758 0.000047
H -1.073878 2.31717 0.000072
H -3.110556 0.845065 0.000004
C 1.811409 0.905362 -0.000152
C 2.020386 -0.664896 0.000149
H 2.199793 1.411108 -0.890898
H 2.522469 -1.059563 -0.889879
H 2.199865 1.411405 0.890387
H 2.522313 -1.059296 0.89039

E(B3LYP/6-31G(d)): -308.292044335
H(B3LYP/6-31G(d)): -308.175281
G(B3LYP/6-31G(d)): -308.212046

4,5-indolyne:

C 0.105227 0.588284 0.000144
C 0.301656 -0.842361 -0.000068

C -0.933915 -1.491159 -0.000379
C -2.042295 -0.920909 -0.000515
C -2.332515 0.444941 -0.000372
C -1.158774 1.215522 0.000051
C 2.320193 0.143452 -0.000016
C 1.708304 -1.086073 0.000422
H 3.37233 0.392029 -0.000094
H 2.205972 -2.045073 0.000651
N 1.369823 1.144486 0.000493
H -1.23056 2.300708 0.000262
H -3.317408 0.898983 -0.000484
H 1.573623 2.131769 0.000615

E(B3LYP/6-31G(d)): -362.478194214
H(B3LYP/6-31G(d)): -362.365973
G(B3LYP/6-31G(d)): -362.403602

4,5-NBOC-indolyne:

C -1.818782 -0.089011 0.000048
C -2.694733 1.050287 -0.000036
C -4.031554 0.659091 -0.000101
C -4.394453 -0.53502 -0.000098
C -3.644815 -1.706106 -0.000031
C -2.265682 -1.424813 0.00006
C -0.583685 1.831438 0.000115
C -1.883187 2.234421 -0.000029
H 0.327875 2.405832 0.000192
H -2.229341 3.258365 -0.00008
N -0.510533 0.430091 0.000119
H -1.544755 -2.232418 0.000124
H -4.022032 -2.72248 -0.000032
C 0.668048 -0.328087 0.000145
O 0.676391 -1.542256 0.00008
O 1.734023 0.485791 -0.00014
C 3.112355 -0.058752 -0.000045
C 3.346464 -0.874356 1.274499
H 2.728807 -1.773608 1.290681
H 4.399732 -1.171647 1.326351
H 3.120643 -0.271121 2.160509
C 3.346416 -0.874676 -1.274405
H 4.39971 -1.17186 -1.326356
H 2.72886 -1.774013 -1.290238
H 3.120356 -0.271697 -2.160525
C 3.963593 1.212481 -0.000178
H 3.757175 1.817714 0.888351
H 5.026223 0.9492 -0.000073
H 3.757275 1.817433 -0.888918

E(B3LYP/6-31G(d)): -708.312022336

H(B3LYP/6-31G(d)): -708.06404
G(B3LYP/6-31G(d)): -708.121068

5,6-indolyne:

C -0.116141 -0.682478 0.000011
C -0.121539 0.760578 0.000021
C 1.100242 1.490987 -0.000143
C 2.157449 0.610774 -0.000289
C 2.160224 -0.64494 -0.000292
C 1.058783 -1.475692 -0.000149
C -2.262599 0.028036 0.000226
C -1.501313 1.16537 0.00028
H 1.138642 2.575562 -0.000121
H -3.33768 -0.090282 0.000319
H -1.876643 2.179338 0.0004
N -1.438096 -1.082648 0.000185
H 1.045204 -2.561929 -0.00015
H -1.753492 -2.039969 0.000266

E(B3LYP/6-31G(d)): -362.475380989
H(B3LYP/6-31G(d)): -362.363262
G(B3LYP/6-31G(d)): -362.400959

5,6-NBOC-indolyne:

C 1.794844 -0.231084 0.000003
C 2.736104 0.854695 -0.000001
C 4.134921 0.620554 0.000013
C 4.376036 -0.737703 -0.000024
C 3.541019 -1.672178 -0.000014
C 2.161893 -1.598634 0.000026
C 0.651528 1.748561 -0.000024
C 1.967907 2.077639 0.000008
H 4.865317 1.423398 0.00001
H -0.230689 2.367895 -0.000026
H 2.365908 3.083338 0.000035
N 0.511564 0.350689 -0.000007
H 1.440561 -2.402943 0.000035
C -0.693972 -0.356393 -0.000095
O -0.751916 -1.569958 0.000061
O -1.72699 0.500503 -0.000328
C -3.125157 0.011292 0.00001
C -3.391573 -0.794505 1.274557
H -4.456046 -1.048587 1.327389
H -2.810599 -1.717853 1.289247
H -3.140171 -0.201376 2.160521
C -3.391827 -0.795425 -1.273922
H -2.811286 -1.719065 -1.287834

H -4.456423 -1.048991 -1.326719
H -3.13997 -0.203093 -2.160292
C -3.925992 1.314971 -0.00035
H -4.99829 1.093977 0.00005
H -3.695952 1.91208 0.887936
H -3.69644 1.911286 -0.889293

E(B3LYP/6-31G(d)): -708.310191799
H(B3LYP/6-31G(d)): -708.062226
G(B3LYP/6-31G(d)): -708.119247

6,7-indolyne:

C 0.277881 -0.753756 -0.000114
C 0.097662 0.674941 -0.000103
C -1.204953 1.228287 0.000038
C -2.352604 0.415597 0.000198
C -1.973892 -0.918987 -0.000075
C -0.881006 -1.527996 -0.000086
C 2.312311 0.19849 0.000145
C 1.419595 1.238799 -0.000124
H -1.332668 2.308274 0.000069
H -3.358524 0.817079 0.000229
H 3.393282 0.211226 0.000604
H 1.67828 2.28892 -0.000508
N 1.628739 -1.005206 0.0
H 2.048495 -1.921321 0.00033

E(B3LYP/6-31G(d)): -362.479676227
H(B3LYP/6-31G(d)): -362.367491
G(B3LYP/6-31G(d)): -362.405083

67-NBOC-indolyne:

C -1.411865 -0.075933 -0.000041
C -2.743537 0.456401 -0.000119
C -3.863282 -0.404436 -0.000097
C -3.716679 -1.804907 0.000015
C -2.371496 -2.145135 0.000106
C -1.328144 -1.455978 0.000177
C -1.269774 2.18314 -0.000145
C -2.598961 1.893946 0.000031
H -4.865637 0.017187 -0.000133
H -4.564403 -2.480011 0.000067
H -0.74416 3.12518 -0.000193
H -3.397883 2.623227 0.000086
N -0.521001 0.99837 -0.000069
C 0.883689 0.994914 -0.000054
O 1.527391 2.024395 0.000229

O 1.338422 -0.259008 -0.000258
C 2.790741 -0.551113 -0.00001
C 2.813469 -2.080706 -0.000986
H 3.848651 -2.437478 -0.000149
H 2.307353 -2.475535 0.885361
H 2.309174 -2.474482 -0.888848
C 3.428747 0.007974 1.274685
H 4.474803 -0.313478 1.327592
H 3.397727 1.098692 1.289312
H 2.910904 -0.375633 2.160359
C 3.429855 0.009477 -1.273505
H 4.475477 -0.313341 -1.326595
H 2.911825 -0.372108 -2.159961
H 3.4001 1.100228 -1.286527

E(B3LYP/6-31G(d)): -708.312368242
H(B3LYP/6-31G(d)): -708.064543
G(B3LYP/6-31G(d)): -708.121914