

## Binding Indirect Greenhouse Gases OCS and CS<sub>2</sub> by Nitrogen Heterocyclic Carbenes (NHCs)

M. Merced Montero-Campillo,\* Ibon Alkorta,\* José Elguero

\*[mm.montero@uam.es](mailto:mm.montero@uam.es), [ibon@iqm.csic.es](mailto:ibon@iqm.csic.es)

### Supporting Information

**Table S1**, p. S2-S9. Non-covalent complexes, transition states and products for the reactions between NHC (**1-7**) + CS<sub>2</sub>.

**Table S2**, p. S10-S24. Non-covalent complexes, transition states and products for the reactions between NHC (**1-7**) + OCS. Molecular graphs obtained with QTAIM are also shown.

**Table S3**, p. S24. Dihedral angles (°) for the different NHC-CXY (NHC = (**1-7**)) products.

**Table S4**, p. S25. Chemical bonding analysis (EDA-ADF) for non-covalent complexes.

**Figure S1**, p. S26-S30. Energy paths for the NHC + CXY reactions obtained by IRC calculations.

**Figure S2**, p. S31. CO<sub>2</sub>, OCS and CS<sub>2</sub> LUMO orbitals.

**Figure S3**, p. S32. Stability of the TSs NHC/CXY (NHC=**1-7**, CXY = CS<sub>2</sub>, OCS) versus the stability of the TSs NHC/CO<sub>2</sub>.

**Figure S4**, p. S33. Stability of the TSs NHC/CXY (NHC=**1-7**, CXY = CO<sub>2</sub>, CS<sub>2</sub>, OCS) versus C···C distances.

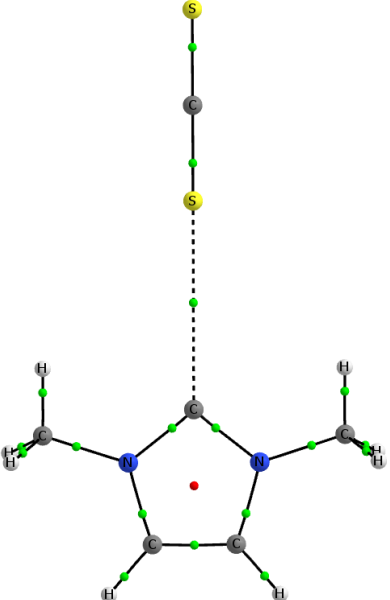
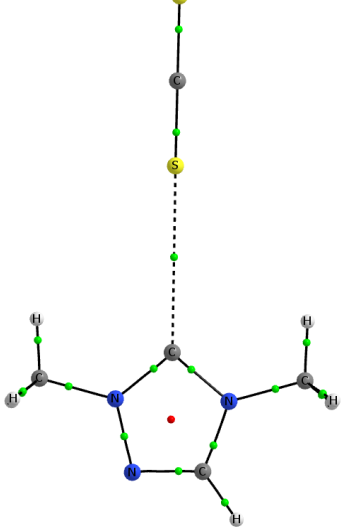
**Figure S5**, p. S34. Relationship between the ΔH of the transition states NHC/CXY and products NHC-CXY (NHC = **1-7**, CXY = CO<sub>2</sub>, OCS, CS<sub>2</sub>) with respect to the energy of the HOMO in the isolated **1-7** carbenes. Results regarding CO<sub>2</sub> were taken from Ref. 3.

**Figure S6**, p. S35 Relationship between the ΔH of the transition states NHC/CXY and products NHC-CXY (NHC = **1-7**, CXY = CO<sub>2</sub>, OCS, CS<sub>2</sub>) with respect to the minimum of the MEP in the isolated **1-7** carbenes.

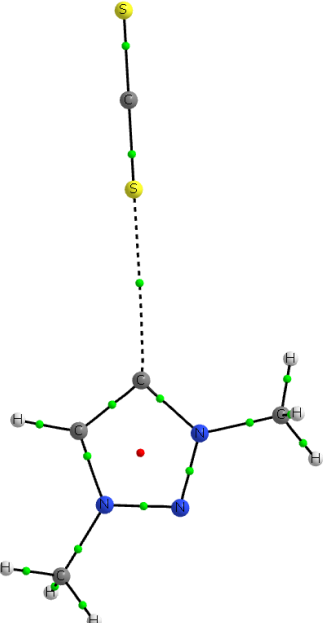
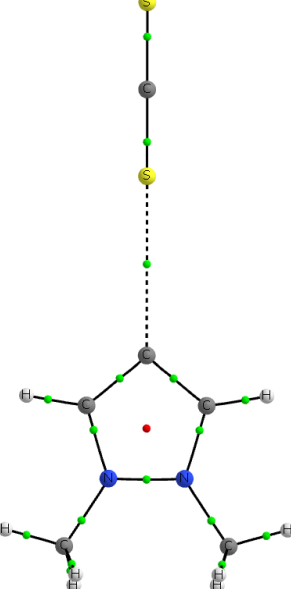
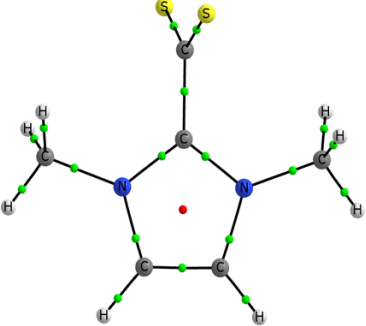
**Figure S7**, p. S36. E<sub>r</sub> (distortion energy) for the different CXY molecules at the NHC/CXY transition states from the distortion-interaction analysis.

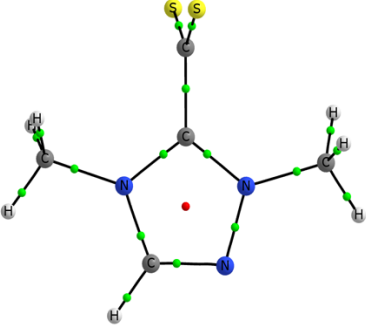
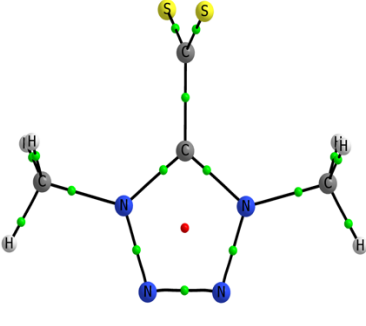
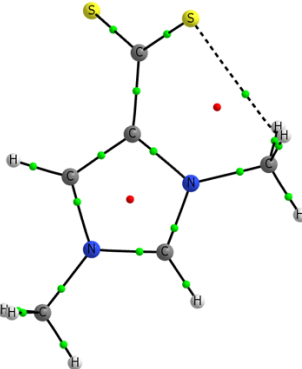
**Figure S8**, p. S37-S42. Distortion-interaction analysis carried out along the path of the NHC + CXY reactions. Negative and positive values of the IRC correspond to the complexes and adducts, respectively.

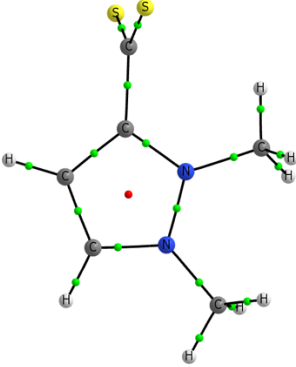
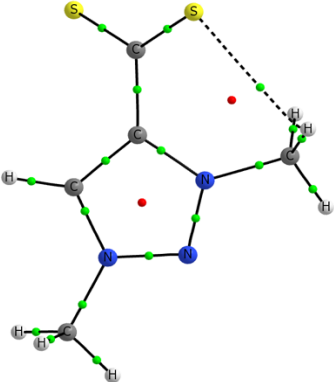
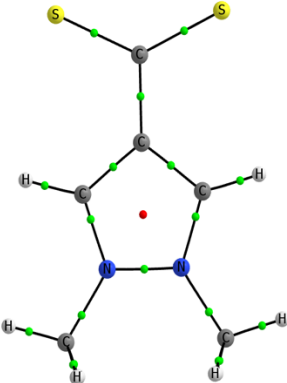
**Table S1.** Non covalent complexes, transition states and products for the reactions between NHC (1-7) + CS<sub>2</sub>. Green and red points indicate the location of bond critical points and ring critical points, respectively, according to their definitions within the QTAIM (Quantum Theory of Atoms in Molecules) framework [see Bader, R.F.W. (1990) Atoms in molecules: a quantum theory. Oxford University Press, New York].

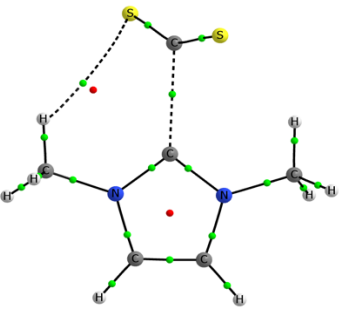
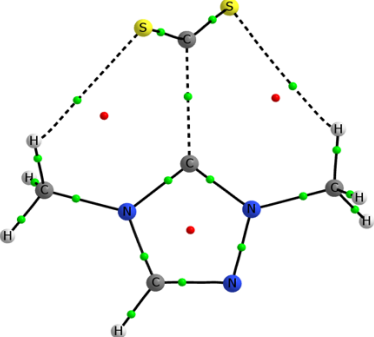
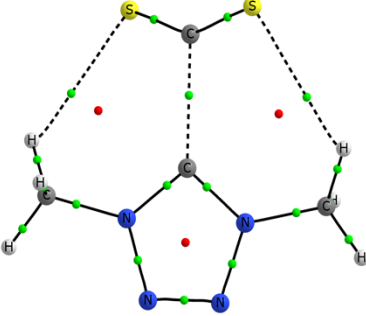
	<p><b>1:CS<sub>2</sub> NIMAG= 0</b>            C,0.,0.,-3.5236036784            S,0.,0.,-1.9666406254            S,0.,0.,-5.0853806438            C,0.,0.,1.4302221212            N,0.,1.0618015956,2.2914374888            N,0.,-1.0618015956,2.2914374888            C,0.,0.6766271681,3.6250097703            C,0.,-0.6766271681,3.6250097703            H,0.,1.3819824841,4.4398014514            H,0.,-1.3819824841,4.4398014514            C,0.,2.441742715,1.844927647            H,0.,2.4386787081,0.7554968721            H,-0.8896373942,2.9695108748,2.2042762304            H,0.8896373942,2.9695108748,2.2042762304            C,0.,-2.441742715,1.844927647            H,0.,-2.4386787081,0.7554968721            H,0.8896373942,-2.9695108748,2.2042762304            H,-0.8896373942,-2.9695108748,2.2042762304</p>
	<p><b>2:CS<sub>2</sub> NIMAG= 0</b>            C,-0.1796422237,3.4829393961,0.            S,-0.1101491282,1.9275702429,0.            S,-0.2495136343,5.0421936944,0.            C,0.0185076152,-1.4923874398,0.            N,1.083001727,-2.3203701159,0.            N,-1.0077714884,-2.4087396406,0.            N,0.7981118056,-3.671857438,0.            C,-0.5008023789,-3.6842076949,0.            H,-1.1038408973,-4.5789708312,0.            C,2.4737309975,-1.9155896233,0.            H,2.5025444347,-0.8269342592,0.            H,2.9799903516,-2.301284764,0.8889018765            H,2.9799903516,-2.301284764,-0.8889018765            C,-2.4171316748,-2.0586718857,0.            H,-2.4875583682,-0.9717637844,0.            H,-2.9168480432,-2.4519658159,-0.8903720913            H,-2.9168480432,-2.4519658159,0.8903720913</p>

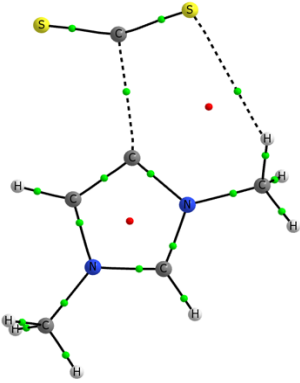
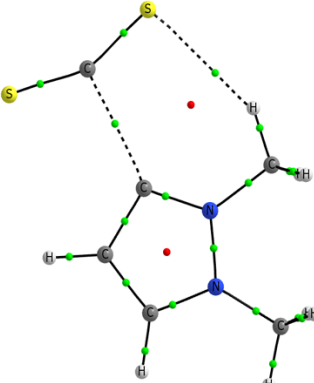
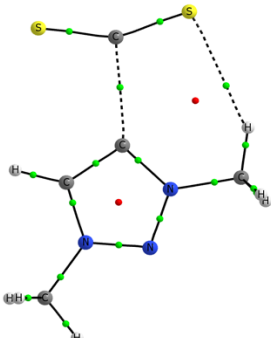
	<p><b>3:CS<sub>2</sub> NIMAG= 0</b>  C,0.,0.,-3.1597797485  S,0.,0.,-1.6028153822  S,0.,0.,-4.7196291969  C,0.,0.,1.854053277  N,0.,1.0286212947,2.7321805538  N,0.,-1.0286212947,2.7321805538  N,0.,0.6336780696,4.0468628242  N,0.,-0.6336780696,4.0468628242  C,0.,2.4469713287,2.4261044486  H,0.,2.5497894406,1.3423453634  H,-0.8899454788,2.922380447,2.84491772  H,0.8899454788,2.922380447,2.84491772  C,0.,-2.4469713287,2.4261044486  H,0.,-2.5497894406,1.3423453634  H,0.8899454788,-2.922380447,2.84491772  H,-0.8899454788,-2.922380447,2.84491772</p>
	<p><b>4:CS<sub>2</sub> NIMAG= 0</b>  C,0.4992866955,-3.672721718,0.1215419701  S,0.3657738194,-2.1224970676,0.0700166744  S,0.6305247595,-5.2311815318,0.1737564123  C,0.0728993366,1.1317683512,-0.0179276176  C,-0.7919301231,3.2603645101,-0.0305748423  N,0.5374607159,3.3800410717,-0.0331131654  N,-1.074772564,1.9500889885,-0.0217113326  C,1.06951483,2.0888087762,-0.0256564792  H,2.1427094365,1.973693656,-0.0266330436  H,-1.4893028606,4.0823616408,-0.0351922473  C,1.2784398218,4.6289411662,-0.0486311369  H,0.5858893119,5.4716144601,-0.0173297496  H,1.9407664658,4.6835991703,0.8195837636  H,1.8822732705,4.7004288166,-0.9576111542  C,-2.4250930777,1.4121541022,-0.013246773  H,-2.5746283089,0.8098853763,0.8854168621  H,-3.157011342,2.2239411105,-0.0333938659  H,-2.5681035446,0.7712338608,-0.8856249648</p>
	<p><b>5:CS<sub>2</sub> NIMAG= 0</b>  C,1.5915802801,3.3796273153,0.020713451  S,1.0470230374,1.9213623779,0.0135958017  S,2.1376195881,4.8448884972,0.0278556021  C,-0.059659666,-1.193871668,-0.0019167539  C,0.7919991879,-2.3457755243,-0.0163932309  C,0.028522425,-3.4896885553,-0.0286335147  N,-1.2896553999,-1.7410595617,-0.0023806987  N,-1.2776610807,-3.1361099599,-0.0280018471  C,-2.4546703688,-3.9718079099,0.0349665418  H,-2.1332714193,-5.0127096689,-0.02347355  H,-3.0019207346,-3.8306682669,0.97368432  H,-3.1310552026,-3.7730393823,-0.8024892907  C,-2.5567666814,-1.0391495698,-0.0103437163  H,-2.3111433411,0.0203430486,0.0176506266  H,-3.1314729997,-1.2527586943,-0.9183494882  H,-3.1653345685,-1.2927961817,0.8645049861  H,1.8709671226,-2.3209582115,-0.0215412088  H,0.2900698215,-4.5380160844,-0.0394480302</p>

	<p><b>6:CS<sub>2</sub> NIMAG= 0</b>  C,-0.1593595232,3.7006740833,0.0978261627  S,-0.0984629464,2.146961922,0.0258267522  S,-0.2195632266,5.2609779713,0.1707738849  C,-0.0203879687,-1.1735380491,-0.0776666324  N,0.637583102,-3.3983001849,-0.0112013488  N,-0.6757521098,-3.3295416794,0.0123381395  N,0.9884786585,-2.1075585325,-0.0652741956  C,-1.1158547329,-2.0388558602,-0.0257570444  H,-2.174984407,-1.8339189075,-0.0150305184  C,-1.4496739096,-4.5604040421,0.0148762792  H,-0.8423514613,-5.3532858699,0.4500472818  H,-2.3496049354,-4.4115751089,0.6137129932  H,-1.7335835306,-4.8352225303,-1.0045412683  C,2.4133735801,-1.8114794244,-0.0578769274  H,2.7929874801,-1.7924921034,0.9676426745  H,2.949100597,-2.5732900707,-0.6264131377  H,2.5460903338,-0.8300316133,-0.509283095</p>
	<p><b>7:CS<sub>2</sub> NIMAG= 0</b>  C,0.,0.,-3.9266381818  S,0.,0.,-2.369784375  S,0.,0.,-5.4929544045  C,0.,0.,0.8498237543  C,0.,1.0694410972,1.7485066425  C,0.,-1.0694410972,1.7485066425  N,0.,0.6786562119,3.0610326642  N,0.,-0.6786562119,3.0610326642  C,0.,-1.4640885696,4.2754595557  H,0.,-2.5131345118,3.977134367  H,0.8923979417,-1.2751666704,4.8814635053  H,-0.8923979417,-1.2751666704,4.8814635053  C,0.,1.4640885696,4.2754595557  H,0.,2.5131345118,3.977134367  H,-0.8923979417,1.2751666704,4.8814635053  H,0.8923979417,1.2751666704,4.8814635053  H,0.,-2.139908469,1.5737180284  H,0.,2.139908469,1.5737180284</p>
	<p><b>1-CS<sub>2</sub> NIMAG= 0</b>  C,0.,0.,1.0450221014  S,1.481449595,0.4318869459,1.7012534267  S,-1.481449595,-0.4318869459,1.7012534267  C,0.,0.,-0.4357181506  N,-0.1515772818,1.073790049,-1.2340698134  N,0.1515772818,-1.073790049,-1.2340698134  C,-0.0937676356,0.6709298036,-2.5574240491  C,0.0937676356,-0.6709298036,-2.5574240491  H,-0.1902447581,1.3718804522,-3.3678371065  H,0.1902447581,-1.3718804522,-3.3678371065  C,-0.3062602845,2.440647392,-0.7503066882  H,-1.0796461563,2.4646655638,0.0193454831  H,0.6353040497,2.7925722312,-0.3233732548  H,-0.6013830272,3.0726932812,-1.588084473  C,0.3062602845,-2.440647392,-0.7503066882  H,1.0796461563,-2.4646655638,0.0193454831  H,-0.6353040497,-2.7925722312,-0.3233732548  H,0.6013830272,-3.0726932812,-1.588084473</p>

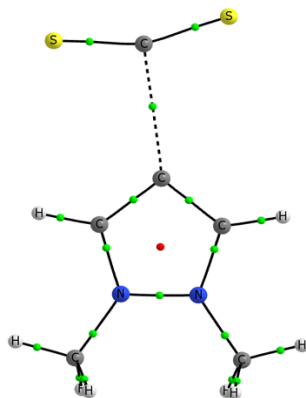
	<p><b>2-CS<sub>2</sub> NIMAG= 0</b>  C,0.0857413292,-1.0397037443,-0.078998073  S,0.4320718733,-1.5761865594,-1.6267897775  S,-0.1821499319,-1.78475285,1.3973653953  C,-0.0239451509,0.4319730063,-0.0011055068  N,0.9600250314,1.3210521089,0.1557918812  N,-1.1622308249,1.162531946,-0.0800003602  N,0.4931915397,2.6071433198,0.1752721546  C,-0.7935762719,2.4769170297,0.0324534579  H,-1.495920196,3.2939276745,0.0064799088  C,2.382818875,1.037171797,0.2520394126  H,2.8655679843,1.9262631161,0.6541701232  H,2.5289631802,0.186827013,0.9197786117  H,2.7818464824,0.7981436839,-0.7364252661  C,-2.5039085845,0.6127697585,-0.2351943454  H,-2.5374836293,-0.0080152952,-1.1325065189  H,-2.749666502,0.0029283892,0.6363452545  H,-3.2076362042,1.4400086059,-0.328676352</p>
	<p><b>3-CS<sub>2</sub> NIMAG= 0</b>  C,0.,0.,1.5674948255  S,1.5010752822,0.3823350302,2.1998446218  S,-1.5010752822,-0.3823350302,2.1998446218  C,0.,0.,0.0918496333  N,-0.1053418194,1.0493634362,-0.7357830585  N,0.1053418194,-1.0493634362,-0.7357830585  N,-0.0634457397,0.6329233512,-2.0291503924  N,0.0634457397,-0.6329233512,-2.0291503924  C,-0.2244512175,2.4559200723,-0.3845925613  H,-1.1178489347,2.5998223655,0.2260249211  H,0.6598796783,2.7584129728,0.1796735937  H,-0.3023580072,3.01535364,-1.3153433082  C,0.2244512175,-2.4559200723,-0.3845925613  H,1.1178489347,-2.5998223655,0.2260249211  H,-0.6598796783,-2.7584129728,0.1796735937  H,0.3023580072,-3.01535364,-1.3153433082</p>
	<p><b>4-CS<sub>2</sub> NIMAG= 0</b>  C,0.5004218187,1.857732606,0.3123481789  S,-0.2263493399,2.9775717477,-0.7058281255  S,1.6575663646,2.0448737172,1.5248695027  C,-0.0021369409,0.4713516914,0.1402749478  C,0.0158925103,-1.7317685497,-0.1878136818  N,-1.2541580835,-1.3638614091,0.0004422963  N,0.7926100697,-0.6467234971,-0.1033930669  C,-1.2888260601,0.0001763253,0.1959008996  H,-2.2063560353,0.5408544416,0.3436963825  H,0.3542602376,-2.7325559722,-0.3933953264  C,-2.4071919243,-2.2534930464,-0.0005140631  H,-2.0809535392,-3.2648391146,-0.2450006647  H,-2.8785232585,-2.2552935423,0.98495296  H,-3.1303552798,-1.9188037572,-0.7472386699  C,2.2446203492,-0.655669293,-0.2746227616  H,2.5193309447,0.0648379485,-1.0462276645  H,2.7137199921,-0.3551853391,0.662618806  H,2.5490961746,-1.6594429573,-0.5760699491</p>

	<p><b>5-CS<sub>2</sub> NIMAG= 0</b>  C,-1.4246821764,0.0772789747,0.0641327033  S,-2.0913118276,-0.3116607834,1.5511716235  S,-2.0372709936,0.1735311887,-1.493968095  C,0.0224981015,0.393225313,0.1385165213  C,0.6805610841,1.6106908344,0.3970412864  C,2.0274516863,1.3529207285,0.317902621  N,0.9764550868,-0.5384487611,-0.0694131563  N,2.2142970177,0.0477862352,0.0183469774  C,3.4466096334,-0.7082249327,-0.0486294494  H,4.2689083597,0.0063076166,-0.0079698862  H,3.5376069366,-1.401233955,0.7938824829  H,3.5126065787,-1.2643078113,-0.9872800207  C,0.7985753405,-1.9304558752,-0.4407506157  H,-0.2619451384,-2.151239251,-0.3313896064  H,1.0931727379,-2.095210521,-1.4809265824  H,1.3728795107,-2.5788580928,0.2248225295  H,0.1986010941,2.5497091504,0.6054048  H,2.881338968,1.9975759421,0.4541058667</p>
	<p><b>6-CS<sub>2</sub> NIMAG= 0</b>  C,0.4829287738,1.9213358763,0.0093971228  S,-0.2327017352,2.8625016512,-1.1825404162  S,1.614651226,2.2749310757,1.2011084219  C,-0.0204814015,0.5267942359,0.0160882666  N,0.0094373587,-1.7226530097,-0.0600903545  N,-1.2326042398,-1.2941752945,0.0538148108  N,0.7333952627,-0.6107573152,-0.0716431133  C,-1.3174779527,0.0532825091,0.0947442323  H,-2.2467819934,0.5911964662,0.1546312081  C,-2.3154783948,-2.2677020451,0.1203607494  H,-1.8885002664,-3.2512140299,-0.0682837831  H,-2.7732776911,-2.2428031787,1.1113621001  H,-3.0628076778,-2.0306829492,-0.6386956321  C,2.184228403,-0.7187455044,-0.1896694386  H,2.6374912492,-0.3297570069,0.7228331269  H,2.4188009657,-1.7699818361,-0.3499748377  H,2.5179461139,-0.1131746449,-1.0334424636</p>
	<p><b>7-CS<sub>2</sub> NIMAG= 0</b>  C,0.,0.,2.3046994773  S,0.0012652564,1.5265888773,3.0201658206  S,-0.0012652564,-1.5265888773,3.0201658206  C,0.,0.,0.816023997  C,0.0009195646,1.1019759886,-0.0361044518  C,-0.0009195646,-1.1019759886,-0.0361044518  N,0.0005648084,0.6824142403,-1.3170746383  N,-0.0005648084,-0.6824142403,-1.3170746383  C,-0.001270989,-1.470507004,-2.5356344414  H,-0.002006591,-2.5185546567,-2.2384606043  H,-0.895583135,-1.2711709884,-3.1322643779  H,0.8932113175,-1.2724824739,-3.1324431972  C,0.001270989,1.470507004,-2.5356344414  H,0.002006591,2.5185546567,-2.2384606043  H,0.895583135,1.2711709884,-3.1322643779  H,-0.8932113175,1.2724824739,-3.1324431972  H,0.0017969575,2.1475961542,0.2285455478  H,-0.0017969575,-2.1475961542,0.2285455478</p>

	<p><b>1/CS<sub>2</sub>, NIMAG= 1</b>  C,0.1318620436,-0.0370327698,1.7210548066  S,1.6219095108,0.5000057494,1.9166669271  S,-1.2511728705,-0.5877504633,2.2912691062  C,-0.1060829363,0.0003230884,-0.5644194404  N,-0.0407805672,1.0752279678,-1.3873805122  N,-0.0511747093,-1.0606430256,-1.4059027477  C,0.0536323119,0.6949979741,-2.7195357585  C,0.048475697,-0.658414719,-2.7314438358  H,0.1060665463,1.4085320193,-3.5248977094  H,0.1044442093,-1.3584031869,-3.5483564891  C,-0.0778326936,2.4550775907,-0.9301025572  H,-0.1468571724,2.4541194606,0.1560962339  H,0.8331163327,2.9811620651,-1.2295278384  H,-0.9451961749,2.9733400473,-1.3493085856  C,-0.0645902553,-2.4478805075,-0.9682050333  H,-0.3026988773,-2.4695791282,0.0941630383  H,-0.8247386707,-3.0089594737,-1.51882877  H,0.911618276,-2.9141226886,-1.1316028346</p>
	<p><b>2/CS<sub>2</sub>, NIMAG= 1</b>  C,-2.1638348618,-0.2244512437,0.1793822651  S,-2.5293073505,-1.0175351885,1.5142454295  S,-2.5977992515,0.4935039656,-1.1831746383  C,0.0619515518,-0.0147872133,0.1469698503  N,0.9764781051,-0.9640333802,-0.080949849  N,0.786332519,1.1324606926,0.0097179221  N,2.2406582721,-0.4868149208,-0.3580874276  C,2.0840387496,0.8017683752,-0.2896842188  H,2.8690352802,1.524755951,-0.445853764  C,0.7567892476,-2.3991223975,-0.0869006302  H,-0.2537612587,-2.5877538644,0.2725721476  H,0.8745120803,-2.7916174985,-1.0998918089  H,1.4839206811,-2.8798494462,0.5705041381  C,0.2584104785,2.4787332088,0.1835633317  H,0.9634304638,3.1952099837,-0.2418862667  H,-0.6984839961,2.5563853896,-0.3342536205  H,0.1148468696,2.7009799565,1.2437271396</p>
	<p><b>3/CS<sub>2</sub>, NIMAG= 1</b>  C,-0.0267930196,0.0015600544,2.1501231423  S,1.2642472157,0.8438504621,2.5833041291  S,-1.3275092253,-0.8401658771,2.5544988055  C,-0.0017723582,0.0001012609,-0.0162677168  N,-0.0314034729,1.036476411,-0.8669408258  N,0.0474623791,-1.0374112334,-0.8646425815  N,-0.0036464077,0.6324520817,-2.1772861788  N,0.0499518739,-0.6351417021,-2.1758192432  C,-0.1167925777,2.453498204,-0.5492637035  H,0.4416267265,2.6348218933,0.3692139844  H,0.3164658065,3.0130827281,-1.3779960956  H,-1.1596310041,2.7487697039,-0.4116491565  C,0.1254772705,-2.4540050101,-0.543183038  H,-0.4539969526,-2.6341097352,0.3624015721  H,-0.288543561,-3.0147055733,-1.3809459346  H,1.1648573069,-2.7490736683,-0.381138193</p>

	<p><b>4/CS<sub>2</sub> NIMAG= 1</b>  C,-0.7913741762,-1.558197288,-0.2239122457  S,-2.2805625339,-1.3053764616,0.2525493358  S,0.409739047,-2.4084100934,-0.8195977462  C,0.1480235124,0.67854621,0.1354642264  C,1.3848118825,2.5850565299,0.0210539783  N,0.0991491264,2.9472213152,0.0124072413  N,1.4274738291,1.2473442439,0.0887340862  C,-0.6653726407,1.7861339261,0.0795667467  H,-1.7418100309,1.8519938895,0.0783751661  H,2.2225621841,3.2624677178,-0.0179688029  C,-0.3986742766,4.3108450813,-0.067396625  H,0.4399609955,5.0073219943,-0.1103960212  H,-1.010676676,4.4354601597,-0.9644460416  H,-1.0064797767,4.5402478251,0.8116328241  C,2.6557938602,0.4674844148,0.1592219269  H,2.529901823,-0.4311122378,-0.444919162  H,3.4955124336,1.0568296327,-0.21673829  H,2.8558865373,0.1685898005,1.1916357729</p>
	<p><b>5/CS<sub>2</sub> NIMAG= 1</b>  C,-0.0116237065,2.8124490819,0.  S,1.5626245223,3.0434039115,0.  S,-1.5249691949,3.2807505124,0.  C,-0.3347807928,0.4047017661,0.  C,-1.6333873272,-0.1661347172,0.  C,-1.5121626005,-1.537512995,0.  N,0.4916179857,-0.6522647008,0.  N,-0.1982442236,-1.8583776772,0.  C,0.4330444653,-3.1597299861,0.  H,-0.3547698784,-3.913928701,0.  H,1.0518130954,-3.3031400503,-0.8913872064  H,1.0518130954,-3.3031400503,0.8913872064  C,1.941992388,-0.6362851739,0.  H,2.3446638707,-1.1248022742,-0.8930243409  H,2.2333721784,0.4140256261,0.  H,2.3446638707,-1.1248022742,0.8930243409  H,-2.5555711055,0.3935285695,0.  H,-2.2485071247,-2.3276503941,0.</p>
	<p><b>6/CS<sub>2</sub> NIMAG= 1</b>  C,-0.7541757966,-1.5098405122,-0.1715516065  S,-2.315345856,-1.2041921996,-0.1882320763  S,0.4947286787,-2.4969212687,-0.1975309492  C,0.11655476,0.6724184999,-0.0420746188  N,1.3564166214,2.5983576079,0.0825162732  N,0.0737065762,2.8977476671,0.050486163  N,1.3467578053,1.2650222981,0.0255714232  C,-0.7088434782,1.7884965057,-0.0244286923  H,-1.7837127573,1.860606665,-0.0578843692  C,-0.3275327031,4.2970026877,0.0711369141  H,0.5462197318,4.8971693905,0.3201226752  H,-0.7114069957,4.5908726406,-0.9087226758  H,-1.1048204005,4.439708189,0.8240657871  C,2.6314512852,0.5757243281,0.0498830052  H,2.4246142829,-0.4906507028,-0.0284013577  H,3.2450265846,0.9069687162,-0.7903857525  H,3.1514017059,0.7926822861,0.985429866</p>

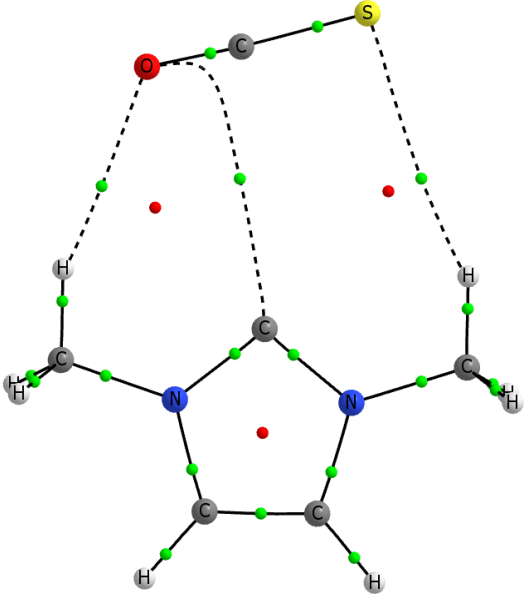
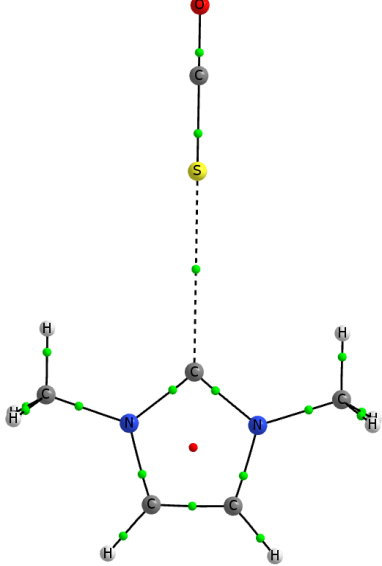


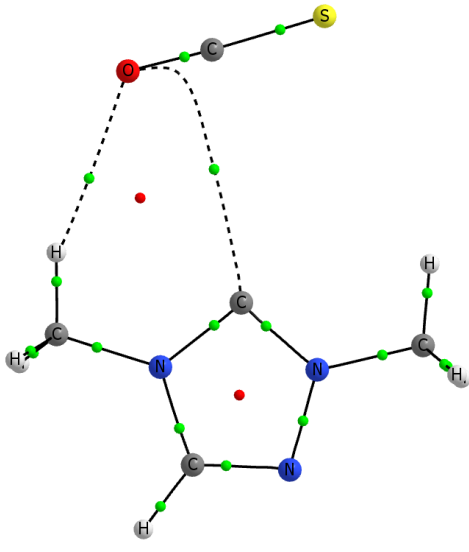
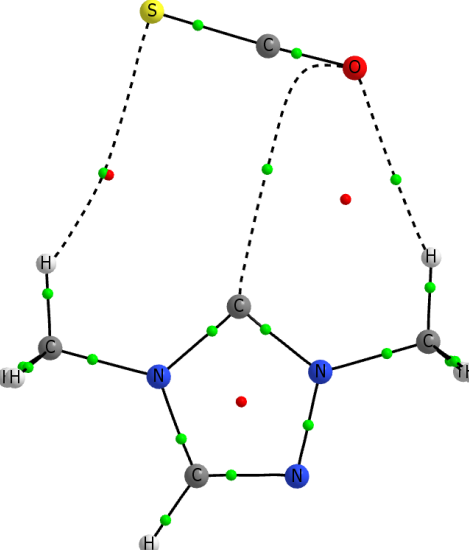
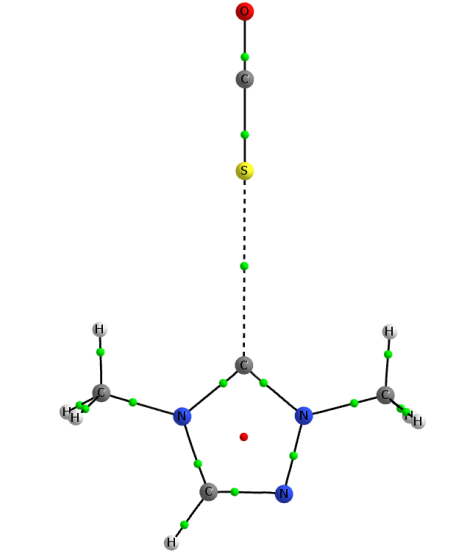


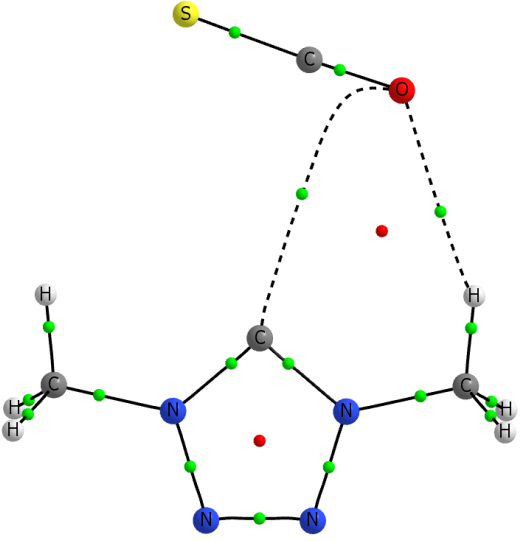
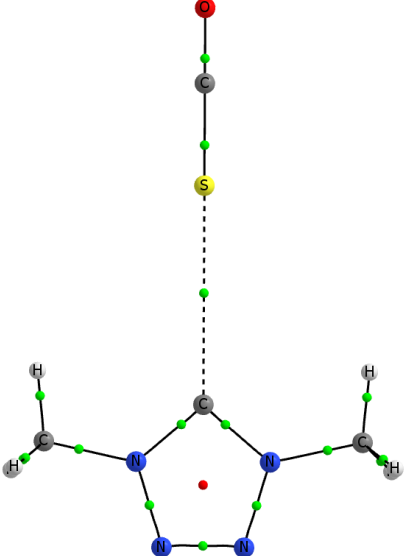
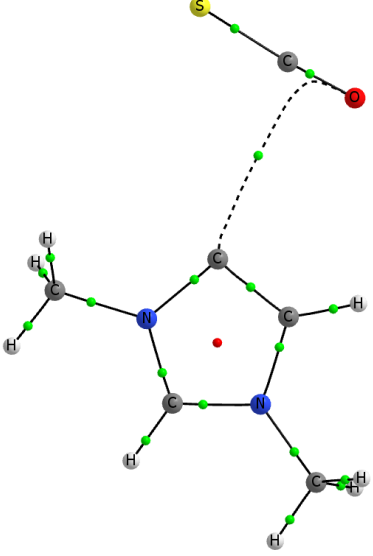
7/CS<sub>2</sub>, NIMAG= 1

C,-0.000020303,0.1248963437,3.1987135863  
 S,0.0000835847,1.7034802976,3.2998256391  
 S,-0.000084837,-1.379341457,3.6769320496  
 C,-0.0000100966,-0.1230892525,0.6557704876  
 C,0.0000519515,0.9851526224,-0.1850060786  
 C,-0.0000647266,-1.1640318508,-0.2679824485  
 N,0.0000360604,0.6411557401,-1.5052926877  
 N,-0.0000376804,-0.7171977096,-1.5593917109  
 C,-0.0000750515,-1.453368333,-2.8060994963  
 H,-0.0001332317,-2.5134082765,-2.5507230042  
 H,-0.8928877098,-1.2384757902,-3.4020735744  
 H,0.8927635089,-1.2385728791,-3.4020697705  
 C,0.0000838387,1.4734683976,-2.6901531444  
 H,0.0001394748,2.5099762345,-2.3518657606  
 H,0.8929088238,1.3056759545,-3.3009427151  
 H,-0.8927567852,1.3057730442,-3.300946519  
 H,0.0001089134,2.0422197123,0.0556600132  
 H,-0.000123415,-2.2376511875,-0.1206338042

**Table S2.** Non covalent complexes, transition states and products for the reactions between NHC (1-7) + OCS. Green and red points indicate the location of bond critical points and ring critical points, respectively, according to their definitions within the QTAIM (Quantum Theory of Atoms in Molecules) framework [see Bader, R.F.W. (1990) Atoms in molecules: a quantum theory. Oxford University Press, New York].

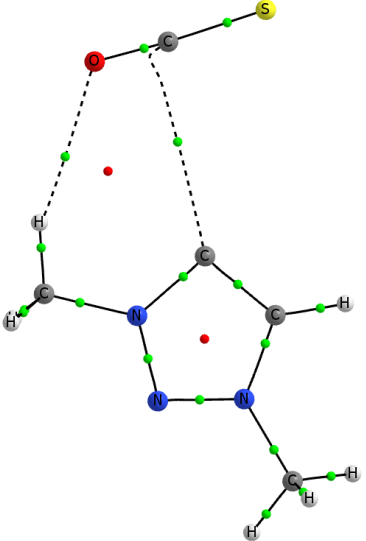
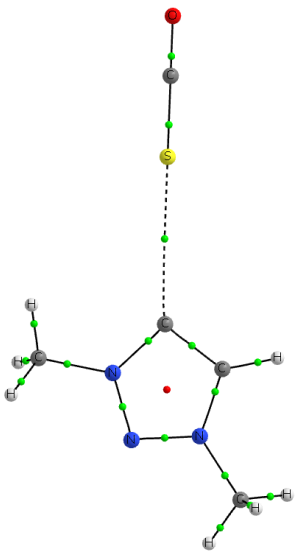
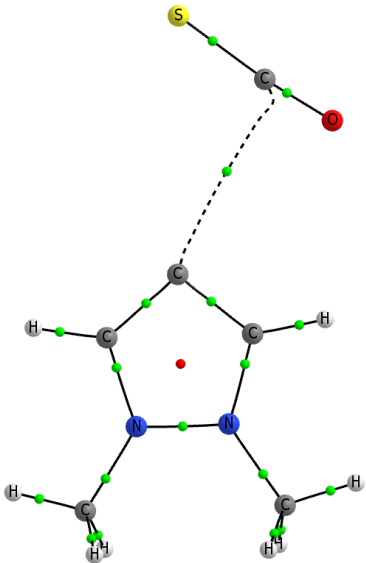
	<p>1:OCS (TB) NIMAG= 0            C,-0.0064507169,-0.2220037167,3.1294331434            S,0.0362961435,1.2961664392,3.5182491006            O,-0.0382963128,-1.3548632008,2.8962537722            C,0.0013141189,0.0436294227,-0.2521406981            N,0.0310738269,1.0827688799,-1.1417096026            N,-0.0297644894,-1.0388234524,-1.0881328134            C,0.0189945514,0.6648000457,-2.4651749589            C,-0.0197763142,-0.6876425723,-2.4309827448            H,0.0385672646,1.3490610732,-3.2976094878            H,-0.0406225236,-1.4129342296,-3.2278884765            C,0.0709645125,2.4720164274,-0.7280200737            H,0.0716210114,2.4917184313,0.3613731407            H,0.9750593545,2.9661396132,-1.099524162            H,-0.8033765833,3.0171616777,-1.0993750464            C,-0.0689467762,-2.4065795275,-0.6058561645            H,-0.0679650478,-2.3744528086,0.4828117278            H,-0.9734012669,-2.9175945984,-0.952769702            H,0.8047092474,-2.9685679041,-0.9528678667</p>
	<p>1:OCS (YB) NIMAG= 0            C,0.,0.,-3.4799372909            S,0.,0.,-1.9076110587            O,0.,0.,-4.6404556376            C,0.,0.,1.3943122329            N,0.,1.0619474917,2.2547798028            N,0.,-1.0619474917,2.2547798028            C,0.,0.6766569693,3.5882887115            C,0.,-0.6766569693,3.5882887115            H,0.,1.3820647369,4.4029998331            H,0.,-1.3820647369,4.4029998331            C,0.,2.4420740443,1.8083561184            H,0.,2.4395701041,0.7189183633            H,-0.8896625393,2.9695323497,2.168013663            H,0.8896625393,2.9695323497,2.168013663            C,0.,-2.4420740443,1.8083561184            H,0.,-2.4395701041,0.7189183633            H,0.8896625393,-2.9695323497,2.168013663            H,-0.8896625393,-2.9695323497,2.168013663</p>

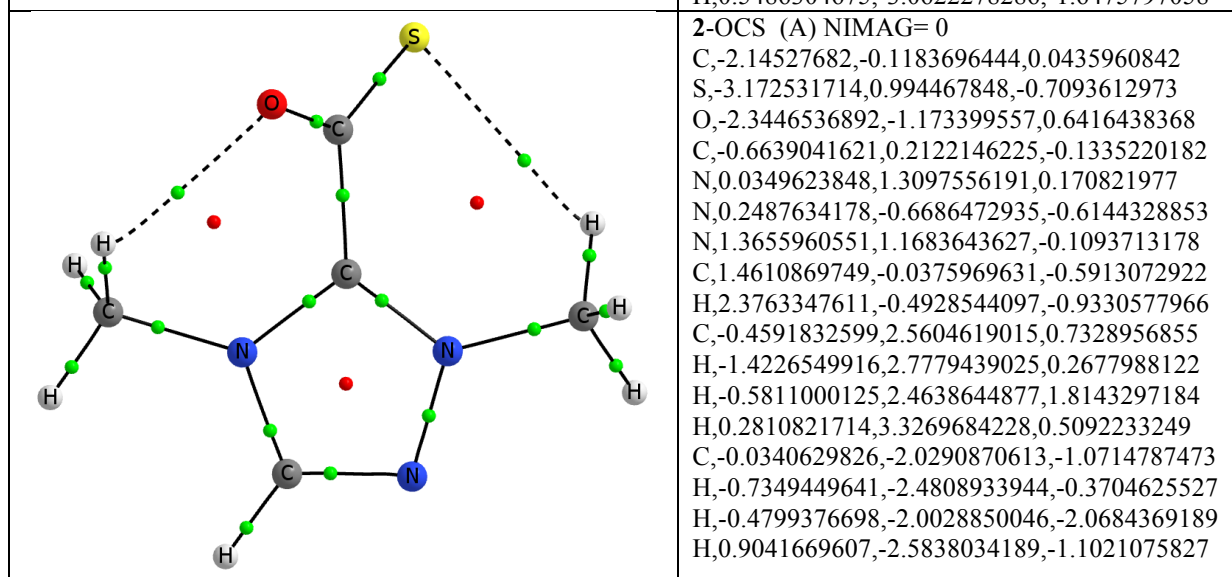
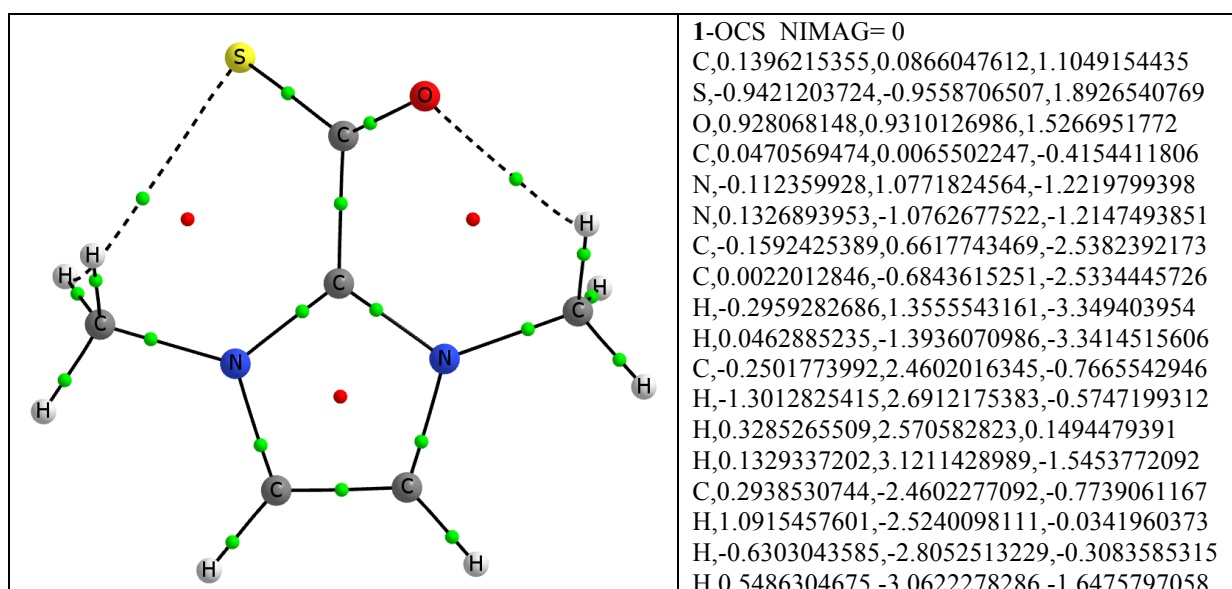
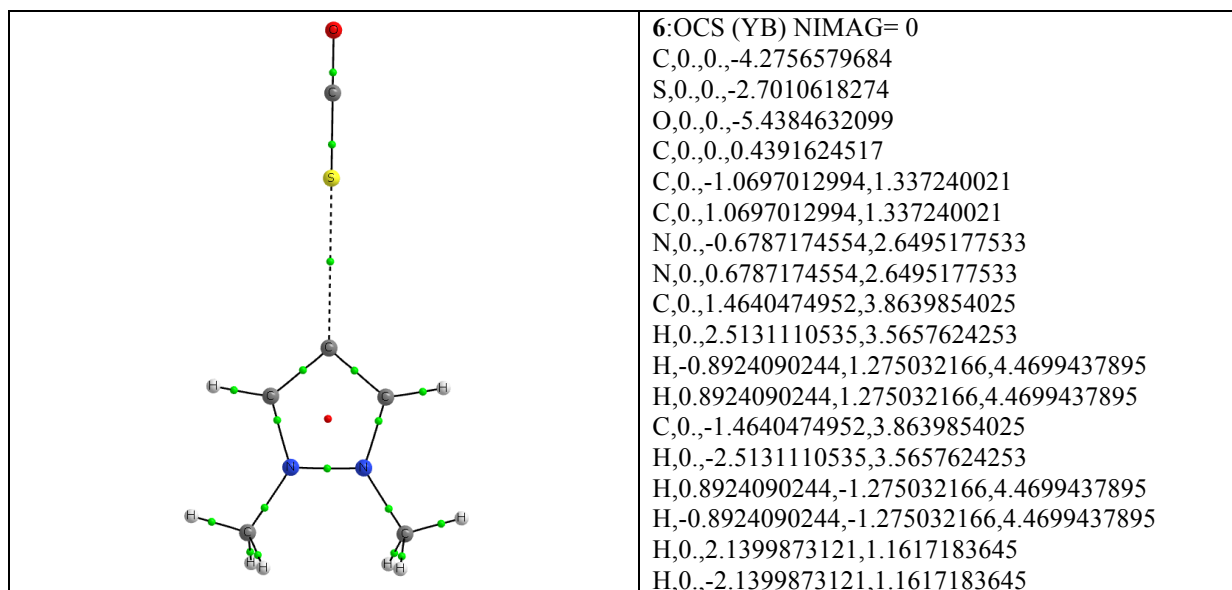
	<p>2:OCS (TB-A) NIMAG= 0  C,-3.1092088768,-0.2804531411,0.  S,-3.536842621,1.2267132996,0.  O,-2.8394612275,-1.4063294105,0.  C,0.263026814,0.0700856691,0.  N,1.166805538,1.0719454285,0.  N,1.1045850388,-1.0194043381,0.  N,2.4946768631,0.6910044711,0.  C,2.4130527908,-0.605554388,0.  H,3.2621281144,-1.2714715649,0.  C,0.8611391744,2.4873791642,0.  H,-0.2231077333,2.5904826452,0.  H,1.2812688755,2.9659389479,0.8888211734  H,1.2812688755,2.9659389479,-0.8888211734  C,0.6523196999,-2.4000002875,0.  H,-0.4366785971,-2.3901566006,0.  H,1.0098472604,-2.9266734723,-0.890099167  H,1.0098472604,-2.9266734723,0.890099167</p>
	<p>2:OCS (TB-B) NIMAG= 0  C,-3.112391842,0.2667249823,0.  S,-3.5367233302,-1.2423735949,0.  O,-2.8461842448,1.3927723723,0.  C,0.2576633995,-0.0593386671,0.  N,1.0843770658,1.0069027758,0.  N,1.177824391,-1.0833890029,0.  N,2.4368728561,0.7251893107,0.  C,2.452073393,-0.5737517698,0.  H,3.3482958613,-1.1747208792,0.  C,0.6741635316,2.3964532471,0.  H,-0.4144305148,2.4198274732,0.  H,1.0593385147,2.9039081605,0.8886247663  H,1.0593385147,2.9039081605,-0.8886247663  C,0.8287190345,-2.4926137825,0.  H,-0.2584456787,-2.5612407316,0.  H,1.2220881475,-2.9927430785,-0.8902873631  H,1.2220881475,-2.9927430785,0.8902873631</p>
	<p>2:OCS (YB) NIMAG= 0  C,-0.1774413626,3.4416090177,0.  S,-0.1117848026,1.8713729282,0.  O,-0.2261537655,4.6006375186,0.  C,0.0159914923,-1.454674678,0.  N,1.0814101159,-2.2809679887,0.  N,-1.0095708629,-2.3713493071,0.  N,0.7975756295,-3.6326026005,0.  C,-0.5013508733,-3.6462835888,0.  H,-1.1035501206,-4.5416067804,0.  C,2.4717271588,-1.8744734881,0.  H,2.4993522211,-0.7857791578,0.  H,2.9782594887,-2.2597250991,0.8889168645  H,2.9782594887,-2.2597250991,-0.8889168645  C,-2.4192772652,-2.0222209299,0.  H,-2.4906778542,-0.9353791989,0.  H,-2.9184986407,-2.4160610415,-0.8903832611  H,-2.9184986407,-2.4160610415,0.8903832611</p>

	<p>3:OCS (TB) NIMAG= 0  C,-0.0093803727,-0.3264486565,3.2060777118  S,0.0333930546,1.1673959011,3.6757035595  O,-0.0412999699,-1.441796546,2.8971012235  C,0.0024723613,0.0858207363,-0.168241938  N,0.030638765,1.0684120554,-1.0981409955  N,-0.0282302799,-0.985182544,-0.9947812036  N,0.017460587,0.6085219995,-2.3914164256  N,-0.0188119668,-0.6568364403,-2.3275828688  C,0.0716325283,2.4988877618,-0.8611557747  H,0.076095102,2.651689273,0.2167634349  H,0.9741156716,2.9286870815,-1.3021970355  H,-0.8048382807,2.9796513606,-1.3020508965  C,-0.0683800847,-2.3854886297,-0.6151693703  H,-0.0696026808,-2.4302459987,0.4723992262  H,-0.9719135327,-2.8560247019,-1.0100738443  H,0.8066490983,-2.907042652,-1.0101763173</p>
	<p>3:OCS (TB) NIMAG= 0  C,0.,0.,-3.1204420054  S,0.,0.,-1.5491913161  O,0.,0.,-4.2798631525  C,0.,0.,1.8138929875  N,0.,1.0288548048,2.6916590209  N,0.,-1.0288548048,2.6916590209  N,0.,0.6337005824,4.006019379  N,0.,-0.6337005824,4.006019379  C,0.,2.4470923089,2.3849607247  H,0.,2.5493594621,1.301164216  H,-0.8899340904,2.9226826697,2.8036207538  H,0.8899340904,2.9226826697,2.8036207538  C,0.,-2.4470923089,2.3849607247  H,0.,-2.5493594621,1.301164216  H,0.8899340904,-2.9226826697,2.8036207538  H,-0.8899340904,-2.9226826697,2.8036207538</p>
	<p>4:OCS (TB-A) NIMAG= 0  C,1.9946658516,2.6714047512,-0.057608109  S,3.453756579,2.0938979517,-0.0609267778  O,0.9507187436,3.1701818937,-0.0580735042  C,0.2100738372,0.0436360864,0.0308534145  C,-1.1461782582,-1.8126553494,0.0200530431  N,-1.9465307327,-0.7447225318,-0.0189252151  N,0.1166337919,-1.3629753429,0.0486656584  C,-1.1282991154,0.38673063,-0.0123445104  H,-1.5911786504,1.3611130217,-0.0426444639  H,-1.479181041,-2.8379760565,0.0258665727  C,-3.3974968205,-0.7720573814,-0.0664363973  H,-3.7501562653,-1.8047433232,-0.0619203882  H,-3.8134323528,-0.2525682481,0.8013130991  H,-3.7550845495,-0.2802730139,-0.9753695228  C,1.2838137261,-2.2265712421,0.1116178216  H,1.7872859265,-2.1043666027,1.073858992  H,0.9906289481,-3.2724399001,-0.0138726666  H,1.9805933818,-1.9436103426,-0.6791070461</p>

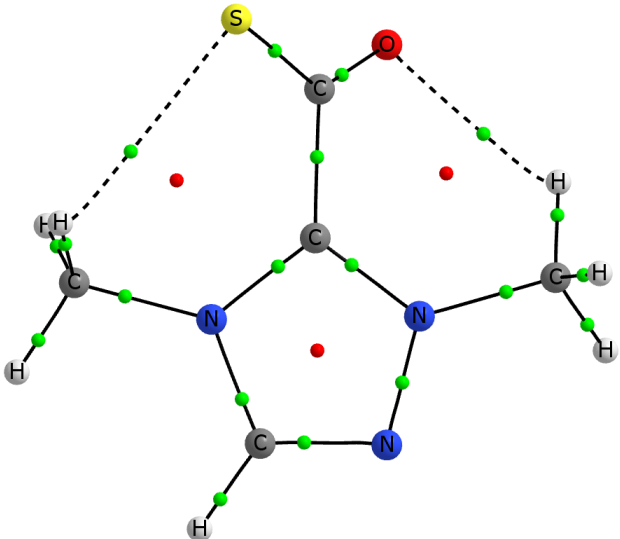
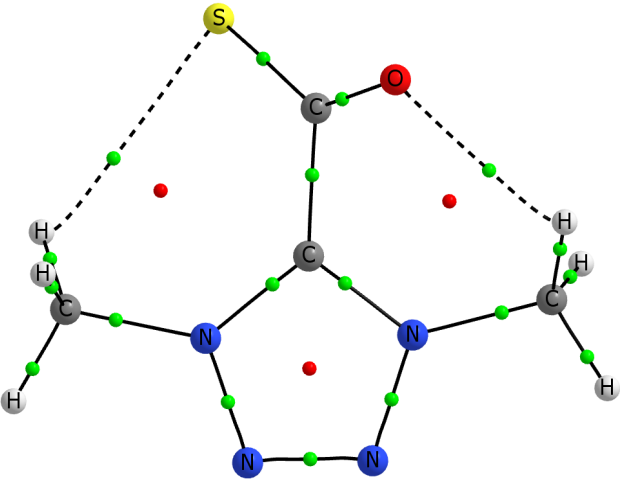
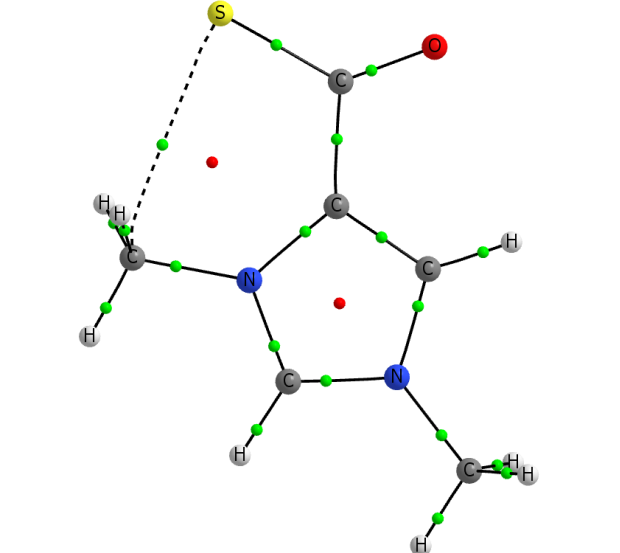
	<p>4:OCS (TB-B) NIMAG= 0  C,2.546923964,2.1619574314,-0.3008474537  S,1.9037297281,3.5334025539,0.1008728206  O,3.086474499,1.1863873752,-0.6147053248  C,-0.0378295167,0.2619743561,0.2244929826  C,-1.1356563677,-1.7466071849,0.0012766309  N,-2.0690171249,-0.7920592114,0.0201063229  N,0.0553997941,-1.1424306676,0.1180007336  C,-1.4089700189,0.4303970318,0.1554292243  H,-1.9986998684,1.3337952429,0.1859025005  H,-1.3308448923,-2.8026359306,-0.093824635  C,-3.5008386347,-1.0023608474,-0.0980986657  H,-3.7134062863,-2.0687789137,-0.1896947948  H,-4.0131677426,-0.6147014632,0.786815173  H,-3.8872693891,-0.4875759134,-0.9821961581  C,1.321707926,-1.8555016754,0.1765393006  H,1.6241064131,-2.0188113323,1.2156537072  H,1.2403100455,-2.8223098508,-0.3281624416  H,2.077680472,-1.2421360006,-0.3125599226</p>
	<p>4:OCS (YB) NIMAG= 0  C,0.4997963654,-3.6414591033,0.1211636457  S,0.3449102932,-2.0761180378,0.0725091998  O,0.6131229821,-4.7974407859,0.1571451012  C,0.0713469505,1.097692733,-0.0138186796  C,-0.7884123403,3.2274149136,-0.0311011129  N,0.5412981002,3.3439717349,-0.0319107062  N,-1.0745029386,1.917892978,-0.0204140979  C,1.0704962172,2.0517173447,-0.0215337127  H,2.1432969924,1.9334082007,-0.0207489422  H,-1.4838657589,4.0510042792,-0.0380103002  C,1.2851404577,4.5911780347,-0.0483603008  H,0.5943731245,5.4354231063,-0.0200452153  H,1.9458885421,4.6460176726,0.821035029  H,1.8908401913,4.6595415481,-0.9563248209  C,-2.4260451951,1.3828213547,-0.0128506709  H,-2.5778354601,0.7821221928,0.8864380808  H,-3.1559128773,2.1963770258,-0.0350399226  H,-2.5692436962,0.740959548,-0.884463264</p>
	<p>5:OCS (TB-A) NIMAG= 0  C,-3.000236803,-0.6571177975,0.0055854897  S,-2.7816517404,-2.2122258843,-0.0054388361  O,-3.2335446304,0.4750214004,0.0141642085  C,0.0192448667,0.4540616892,-0.0057266894  C,0.1423557423,1.882700292,-0.0050766389  C,1.4706637324,2.2364277347,-0.0188404125  N,1.3035654067,0.052627671,-0.0108438531  N,2.2184876226,1.1073625721,-0.0397802595  C,3.648784303,0.9576792808,0.101050141  H,4.1046930008,1.9431707547,-0.0060510792  H,3.9225638437,0.5530060279,1.0826144659  H,4.0568046268,0.3049703038,-0.6765434927  C,1.786974905,-1.3119924695,-0.0547076679  H,0.9003445614,-1.9418907341,-0.0201877467  H,2.3395298474,-1.5153528464,-0.9789359865  H,2.4297117454,-1.5420061571,0.8021737584  H,-0.685408718,2.5751737041,-0.0040254994  H,1.9679626877,3.1958434582,-0.0194299015</p>

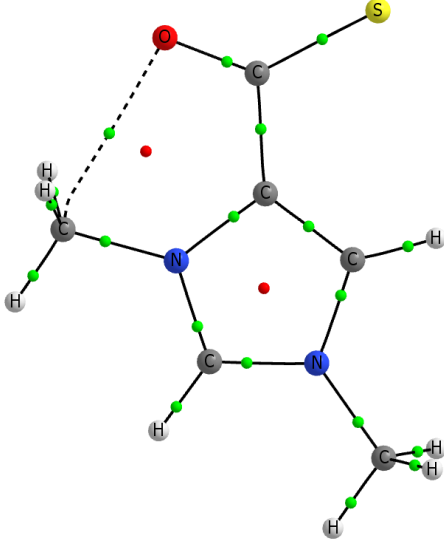
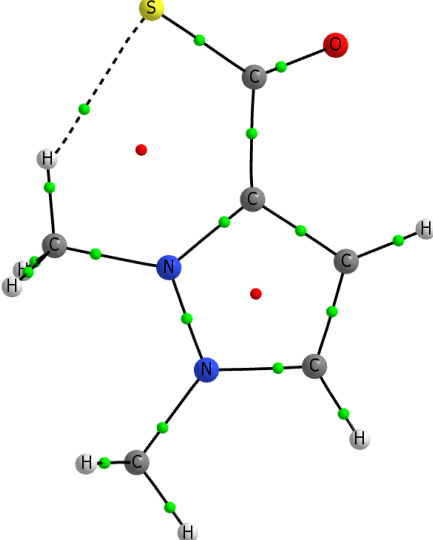
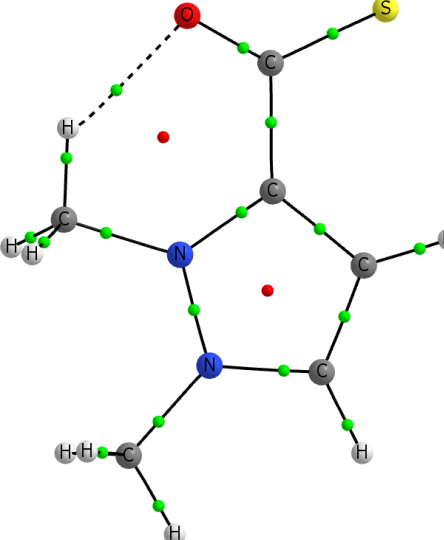
	<p><b>5:OCS (TB-B) NIMAG= 0</b>  C,-2.431926544,-1.6756854657,-0.0006562227  S,-3.6339032023,-0.6716135644,-0.0085214307  O,-1.588774254,-2.4703956377,0.0057303997  C,0.0036468266,0.5277283365,-0.0156049138  C,0.127627628,1.956357585,-0.0046083771  C,1.4562388198,2.3104480584,-0.0049185593  N,1.2888852575,0.1264885418,-0.0145037596  N,2.2034497319,1.1817416764,-0.0246483279  C,3.6352229769,1.0305504889,0.0956126104  H,4.0877911104,2.020469754,0.0199198531  H,3.91909443,0.5920271207,1.0593503027  H,4.0377067474,0.4067241114,-0.7084151633  C,1.7758811439,-1.2377161699,-0.0555646368  H,0.8925446096,-1.8726611228,-0.0368158034  H,2.3444253072,-1.4347345547,-0.9714423329  H,2.4069017579,-1.4670962496,0.8101999292  H,-0.6982174525,2.6512312515,-0.0043071296  H,1.9532491057,3.2699348402,0.004193562</p>
	<p><b>5:OCS (YB) NIMAG= 0</b>  C,1.5261643292,3.3577212376,0.0204151614  S,0.9974359187,1.8762707631,0.0129356337  O,1.9160545662,4.4518302422,0.0259518072  C,-0.0235816194,-1.1774560765,-0.0029808892  C,0.8170747461,-2.3368982122,-0.0173002108  C,0.042267512,-3.4732481544,-0.0275781455  N,-1.2590497864,-1.7119293791,-0.0020418345  N,-1.260334235,-3.106836245,-0.0254602657  C,-2.4456650206,-3.9310258717,0.0332030407  H,-2.133853408,-4.9750522085,-0.0210958485  H,-2.9961712106,-3.7824378805,0.9687898046  H,-3.1158758011,-3.7277907132,-0.8081638405  C,-2.5192418254,-0.9975667517,-0.0079708098  H,-2.2637344719,0.0596789875,0.017621493  H,-3.098202333,-1.20728798,-0.9141403831  H,-3.1278200906,-1.2440154035,0.8689048692  H,1.8961776474,-2.3220663684,-0.0233151801  H,0.2935250824,-4.5240779855,-0.0377744024</p>
	<p><b>6:OCS (TB-A) NIMAG= 0</b>  C,-3.0970661806,-1.3155825948,-0.029358589  S,-4.1100728096,-0.1203836643,-0.0657267412  O,-2.3941816456,-2.2351993663,-0.0031154462  C,-0.2013893548,0.1514197557,0.0092433033  N,1.9834859625,0.9397331027,0.0148460128  N,1.9919088002,-0.3760637674,0.0347818941  N,0.6723853143,1.2131058294,-0.0004192863  C,0.7299216558,-0.8915220785,0.0310000846  H,0.5833688359,-1.959985132,0.0464924078  C,3.2661287047,-1.0752489265,0.0058418211  H,4.0256716807,-0.4385543008,0.458500979  H,3.1730335491,-2.0023350971,0.5734793794  H,3.5513968361,-1.3076724421,-1.0237496913  C,0.2926322495,2.6177447966,-0.0011520698  H,0.5654623655,3.0871374044,0.947876061  H,0.7953336856,3.1434278642,-0.8161888235  H,-0.7865546491,2.6521916166,-0.1349682955</p>

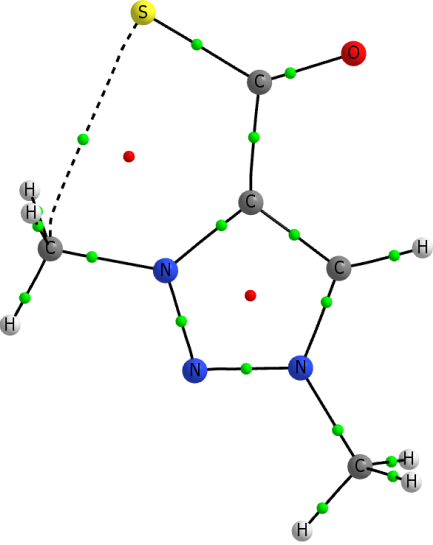
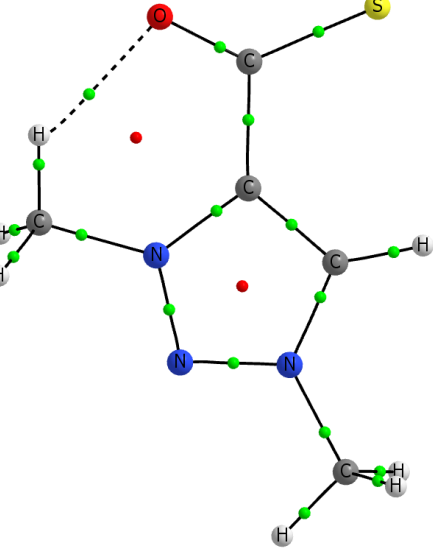
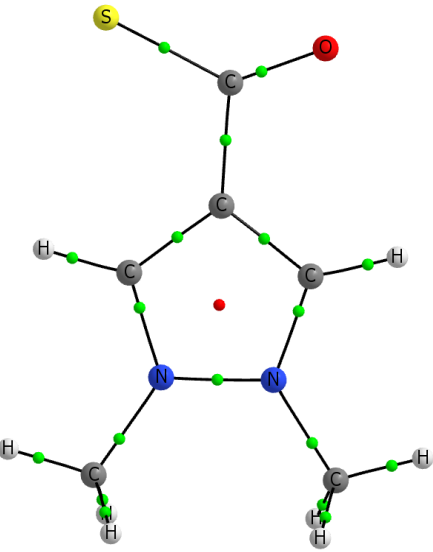
	<p><b>6:OCS (TB-B) NIMAG= 0</b>  C,-3.3974286767,-0.3916077063,-0.0776796754  S,-3.5751621282,-1.9481461646,-0.072101489  O,-3.326960015,0.7643174768,-0.0833277641  C,-0.0843459386,-0.2827321568,-0.0021052383  N,1.933280793,0.8678661155,0.0389988827  N,2.1675298458,-0.4268774651,0.044840086  N,0.5958439155,0.9139207743,0.0108355039  C,1.0119702866,-1.1504615557,0.0195677005  H,1.0551699281,-2.228342101,0.023107105  C,3.5430077666,-0.8968313878,0.0281615221  H,4.1802317503,-0.1260697076,0.4603563403  H,3.6132544524,-1.8108303079,0.6201637281  H,3.8638517652,-1.1033964801,-0.99648769  C,-0.0174050573,2.2343908904,0.0086765814  H,0.2536722348,2.7785112832,0.9170045484  H,0.3188995912,2.8047986631,-0.8607258478  H,-1.0939455133,2.0837028295,-0.0319012937</p>
	<p><b>6:OCS (YB) NIMAG= 0</b>  C,-0.1590686525,3.6673477215,0.094853817  S,-0.0911305088,2.0977770887,0.0281726248  O,-0.2087891953,4.8264884097,0.1443084525  C,-0.0214198974,-1.1372704523,-0.0721486795  N,0.6361774031,-3.3614958205,-0.0096451854  N,-0.6771975932,-3.2925555581,0.0128604553  N,0.9874655428,-2.0708487147,-0.0608754575  C,-1.1172481603,-2.0018583575,-0.0228391097  H,-2.1762074573,-1.7962109393,-0.0126606765  C,-1.4512957934,-4.5233289152,0.0118342775  H,-0.8449024603,-5.3170464623,0.4467760121  H,-2.3523165085,-4.3753600237,0.6092309223  H,-1.7332862527,-4.7962821409,-1.0086087595  C,2.4123793084,-1.7746743934,-0.0520066018  H,2.7906615038,-1.7553665285,0.973972585  H,2.9484643215,-2.5368295171,-0.6197066281  H,2.5457494003,-0.7933653964,-0.5035180487</p>
	<p><b>7:OCS (TB) NIMAG= 0</b>  C,-3.4909198288,-0.8194712164,0.  S,-4.3733944546,0.4771150369,0.  O,-2.9212230915,-1.8281025826,0.  C,-0.5863226338,0.3612583886,0.  C,0.3797185225,1.3696274816,0.  C,0.2422898721,-0.7636799608,0.  N,1.6656500238,0.8953376577,0.  N,1.5772630203,-0.4597472287,0.  C,2.7379160637,-1.3220603461,0.  H,2.3717103754,-2.3494192275,0.  H,3.3556417831,-1.1739296677,-0.8922641956  H,3.3556417831,-1.1739296677,0.8922641956  C,2.9276589748,1.6007864444,0.  H,2.6969670002,2.666838769,0.  H,3.52134445,1.3745259303,0.8922578136  H,3.52134445,1.3745259303,-0.8922578136  H,-0.0074347413,-1.8190807691,0.  H,0.2754271814,2.4494526422,0.</p>





	<p><b>2-OCS (B) NIMAG= 0</b></p> <p>C,-2.1340317765,0.1557352103,-0.1571675731  S,-2.6908044487,-1.2547540459,0.5988767561  O,-2.7073911579,1.1120108265,-0.6696589827  C,-0.6121171217,0.2803797255,-0.0972642796  N,0.0542172252,1.3529083873,0.3439789388  N,0.346855685,-0.6022828197,-0.4726789492  N,1.4082356582,1.1807232668,0.2967498207  C,1.5515387083,-0.0103868267,-0.2095041031  H,2.4990221097,-0.4832361338,-0.4105188589  C,-0.5096559909,2.5939996481,0.8599531557  H,-1.5038883716,2.7066629312,0.429727844  H,-0.5635354363,2.5532942792,1.950568507  H,0.1457750698,3.40934091,0.5547844536  C,0.1455274488,-1.9419477506,-1.0204002197  H,-0.406139512,-2.5400374065,-0.2937990206  H,-0.438353963,-1.8837473638,-1.940028035  H,1.1268984536,-2.368567168,-1.2321324741</p>
	<p><b>3-OCS NIMAG= 0</b></p> <p>C,-0.1162941925,-0.0941257082,1.6258397806  S,1.0027403589,0.9184714431,2.3852984194  O,-0.9206621219,-0.9275511662,2.028862415  C,-0.0286637311,0.0021868437,0.1013580945  N,-0.0800100518,1.0567146703,-0.7243631993  N,0.0857202507,-1.0434544874,-0.7304961033  N,0.0213914922,0.6473146937,-2.0162052838  N,0.1284959621,-0.6218192539,-2.0200152328  C,-0.1810064809,2.4750030564,-0.4036312517  H,-1.1300182039,2.6727002441,0.0972956943  H,0.6390598858,2.73353931,0.2684034899  H,-0.127417291,3.0160175702,-1.3472083514  C,0.1641865461,-2.4600498213,-0.3908537044  H,1.2002407181,-2.7325987335,-0.1775295956  H,-0.4559703258,-2.6177057872,0.491251513  H,-0.2017928149,-3.0246428737,-1.2473145931</p>
	<p><b>4-OCS (A) NIMAG= 0</b></p> <p>C,1.5611044191,1.8891751238,0.0622055927  S,2.9760602177,1.0198554905,0.4550986283  O,1.4085281448,3.0724995013,-0.2310484777  C,0.2365611851,1.1302617966,0.0554767895  C,-1.3910844103,-0.379141374,0.1816285954  N,-1.9531824833,0.7831114543,-0.1669617655  N,-0.0753160413,-0.2045654902,0.323349819  C,-0.9579522889,1.7293472302,-0.2495411157  H,-1.1352848394,2.7565302495,-0.5133085172  H,-1.9186264958,-1.307032612,0.3250950157  C,-3.3713215234,1.0033873469,-0.4171653264  H,-3.9143210542,0.0705808212,-0.2615105179  H,-3.755128303,1.7616915987,0.2686994341  H,-3.5193528805,1.3387205408,-1.4460232987  C,0.8234563475,-1.3001817759,0.7040834413  H,1.3457808975,-1.0391037121,1.6225960992  H,0.2119420674,-2.19747983,0.8310845494  H,1.577836601,-1.4365098296,-0.0685647656</p>

	<p><b>4-OCS (B) NIMAG= 0</b></p> <p>C,1.8232860855,1.6788352639,0.0398480391  S,1.3722730001,3.3196468141,0.0901716736  O,2.933519693,1.1394353569,0.0590114928  C,0.647951669,0.7227437719,-0.0428666692  C,-0.4206622507,-1.2265690791,-0.1614275776  N,-1.3451131447,-0.2589818334,-0.1568948119  N,0.7881532472,-0.6661784867,-0.0936605694  C,-0.7001631421,0.9561233743,-0.083902171  H,-1.2121179661,1.9020772645,-0.0647921953  H,-0.6230699704,-2.2833294181,-0.2115315297  C,-2.7871047479,-0.4585059347,-0.2211236528  H,-3.0015350729,-1.5271123712,-0.2565159757  H,-3.2605670646,-0.0253566799,0.6624871146  H,-3.1887588698,0.0195831287,-1.1171506604  C,2.0386508785,-1.4338777809,-0.077333917  H,2.5920169632,-1.2089110957,0.8316859205  H,1.7799004436,-2.4941273757,-0.1297821816  H,2.6581781988,-1.1383089188,-0.9211063092</p>
	<p><b>5-OCS (A) NIMAG= 0</b></p> <p>C,-2.1480184793,-0.4411933559,-0.1001437157  S,-2.6084742938,-2.0289312094,0.3270816305  O,-2.8267836611,0.522203377,-0.437281744  C,-0.6626064757,-0.071021654,0.0225290879  C,-0.2217147598,1.2255033138,0.335673746  C,1.1523474864,1.19383789,0.3294756709  N,0.4392024079,-0.8294528003,-0.1688443214  N,1.553871087,-0.0563865808,0.0145009325  C,2.9022419985,-0.5665531059,-0.1385735129  H,3.5836356229,0.2715946772,0.0072405542  H,3.1208374439,-1.3361244721,0.6066142444  H,3.0532251758,-0.9767379504,-1.1403679057  C,0.5500735298,-2.228436995,-0.5592987333  H,-0.4658063608,-2.6345352649,-0.4602631025  H,0.9139486737,-2.3090317157,-1.5872656895  H,1.221953321,-2.753059203,0.1234329778  H,-0.8772017388,2.0581900128,0.5198256081  H,1.8869196421,1.9603104167,0.5198900827</p>
	<p><b>5-OCS (B) NIMAG= 0</b></p> <p>C,-1.8124127793,-1.03149362,-0.0265039372  S,-3.2961860058,-0.368885723,-0.5197701037  O,-1.513771931,-2.1924656001,0.2707516663  C,-0.6860435532,0.0023738474,0.0243030684  C,-0.7603143379,1.4036032754,0.074211475  C,0.5315432344,1.8731770696,0.0973273409  N,0.6293230543,-0.323284535,0.027750727  N,1.3789339819,0.819713471,0.0641337601  C,2.8273501994,0.8172613631,0.0133017478  H,3.1531244119,1.8572790451,0.0243226927  H,3.2525267591,0.3041558648,0.8799087923  H,3.1879006345,0.3426891461,-0.9033622299  C,1.2553304199,-1.6400121422,-0.0124182805  H,0.4239954118,-2.3446322555,0.0768724683  H,1.7932805897,-1.7776466502,-0.9544977084  H,1.9421088616,-1.7523939319,0.8302982453  H,-1.6824742906,1.9573243976,0.0735288569  H,0.9249106793,2.8767556379,0.1310283787</p>

	<p><b>6-OCS (A) NIMAG= 0</b>  C,-2.3954185867,-0.6768483632,0.0798189223  S,-3.42133505,0.6798428779,0.1072396162  O,-2.6391330926,-1.8813266563,0.0938445476  C,-0.8896093016,-0.4164011885,0.0290245359  N,1.1615171894,0.4933809335,-0.0441953458  N,1.2603237704,-0.822614289,-0.0382685162  N,-0.1396033065,0.7292527346,-0.0033902767  C,0.053436554,-1.4253042621,0.0052398574  H,-0.0983294839,-2.4899223338,0.0174675004  C,2.5825214667,-1.4360024783,-0.0759751612  H,3.3190695786,-0.6352754673,-0.1149406359  H,2.7313136415,-2.0391078057,0.8216395893  H,2.6669179928,-2.0669141753,-0.9627071219  C,-0.5609594875,2.1330440753,0.000226582  H,-1.1468829786,2.3253559496,0.8975140225  H,0.3505636302,2.7296692897,-0.0353849612  H,-1.2067321562,2.3118881389,-0.8579057847</p>
	<p><b>6-OCS (B) NIMAG= 0</b>  C,-2.4374152448,-0.5038010462,-0.085717102  S,-2.8458013457,-2.1454601574,0.0888964988  O,-3.1431908168,0.4947511681,-0.2357695937  C,-0.9296591355,-0.2671017675,-0.0435949767  N,1.020445707,0.8535779845,0.0256335087  N,1.2496707493,-0.447515722,-0.0088873983  N,-0.299172731,0.9484770311,-0.0018069511  C,0.1121463844,-1.1732995725,-0.0498647646  H,0.0719852928,-2.2479635625,-0.0753116597  C,2.627077228,-0.9258391879,-0.0085023281  H,3.2781908284,-0.0620508675,0.1143571233  H,2.7683100635,-1.6237704668,0.8184079645  H,2.8428402398,-1.4261634894,-0.9545842626  C,-0.9020146988,2.2845320233,0.0438132423  H,-0.7871845396,2.6915610545,1.0505860324  H,-0.381603054,2.919537818,-0.6734755678  H,-1.955438807,2.1487356904,-0.2007411255</p>
	<p><b>7-OCS NIMAG= 0</b>  C,-0.0000668258,-0.0799709461,2.337472005  S,0.0011860294,1.4461542587,3.1089047702  O,-0.0009953556,-1.2259629366,2.7842243556  C,-0.000009685,-0.0101977652,0.8204040628  C,0.0008950359,1.0901740745,-0.0255085105  C,-0.0009164111,-1.1114107659,-0.0260623621  N,0.0005500796,0.6717459974,-1.3070726928  N,-0.0005656666,-0.6938356128,-1.3105625082  C,-0.001260667,-1.477529952,-2.531770976  H,-0.002057072,-2.5267984858,-2.2385069369  H,-0.8954001441,-1.2776518668,-3.1287992754  H,0.8931086587,-1.2790456077,-3.128918389  C,0.0012475549,1.4613192045,-2.5249948941  H,0.0020442934,2.5089180897,-2.2261428909  H,0.8955336191,1.2628816599,-3.121871084  H,-0.8932690123,1.2642778107,-3.1219868649  H,0.0017586033,2.1352696916,0.2437110095  H,-0.0017830347,-2.1583368483,0.231663971</p>

	<p>1/OCS NIMAG= 1  C,0.0190131623,-0.1430002186,2.1250656315  S,-0.9503101949,1.0455887239,2.640001199  O,0.6962742535,-1.081204915,2.3248828991  C,0.0926318553,0.0105510958,-0.1063255893  N,0.0675332731,1.0792167994,-0.9411892699  N,-0.0297526952,-1.0543275546,-0.9393253645  C,-0.0659794799,0.692191709,-2.2661416217  C,-0.1311061677,-0.6597050993,-2.2651386855  H,-0.0947591702,1.4013783447,-3.0764119583  H,-0.2414261298,-1.3636627375,-3.0729456003  C,0.2202293777,2.462023501,-0.5122727363  H,0.1352980617,2.4961150718,0.5725319711  H,1.1943754649,2.8534773961,-0.8207618646  H,-0.5678876256,3.0780262029,-0.9537120637  C,-0.0797051566,-2.4424033761,-0.4999073699  H,0.2110878857,-2.4833197941,0.5475378246  H,-1.089761712,-2.8467801025,-0.6167024014  H,0.6142449978,-3.0441650471,-1.0931159126</p>
	<p>2/OCS (A) NIMAG= 1  C,-2.0442223702,-0.1119092768,-0.0070524152  S,-2.6044436741,1.1145818458,-0.9103315268  O,-2.2557381738,-1.0780693755,0.6334687359  C,0.0972539005,0.0246227405,0.0392137154  N,0.9518223665,1.0547171025,0.0418090923  N,0.9315421062,-1.0540696084,0.0010758731  N,2.2792046593,0.6923002197,0.0096299762  C,2.2276777322,-0.6063313502,-0.020038666  H,3.0889616779,-1.2545726404,-0.0551712259  C,0.6216991617,2.4683087558,0.1109822521  H,-0.454843219,2.5686459444,-0.019782747  H,0.9300088549,2.8743166492,1.0775317211  H,1.1483667272,2.9976352717,-0.6851792121  C,0.5139750427,-2.4515641866,-0.047756232  H,-0.5101100361,-2.5155373897,0.3141657937  H,0.5643816188,-2.8307751686,-1.0721416413  H,1.1691308746,-3.049527635,0.5895765065</p>
	<p>2/OCS (B) NIMAG= 1  C,-2.0258034156,0.0934370429,0.3381037823  S,-2.3739018983,-1.1274156915,1.351479651  O,-2.3707030567,1.0443295096,-0.2621986002  C,0.0855557689,-0.0129726369,-0.0669695947  N,0.9071231813,1.0445970302,-0.0402452788  N,0.9551269558,-1.0616018048,-0.1261013729  N,2.2463094472,0.7277558136,-0.0758127551  C,2.2355231525,-0.5711536313,-0.1331187567  H,3.1166404805,-1.191364267,-0.1798692837  C,0.5274998055,2.4460155098,0.0346316932  H,-0.5529814335,2.5094041199,-0.0776166913  H,0.8347230511,2.8639350174,0.9963993081  H,1.0241314815,2.9946984382,-0.7679959555  C,0.5818996369,-2.4670674212,-0.2317737992  H,0.4913745391,-2.7622143467,-1.2806255933  H,1.346629983,-3.0796542492,0.2501070235  H,-0.3744804324,-2.6079565356,0.271606223</p>

	<p><b>3/OCS NIMAG= 1</b>  C,-0.0561318076,-0.1263773881,2.0607694738  S,0.8464104678,1.1004517425,2.6427190179  O,-0.6856002973,-1.0977530444,2.2959071771  C,-0.0782147406,0.0181838627,0.0144343377  N,-0.0115763043,1.0483506972,-0.8424972836  N,0.028050248,-1.0297461208,-0.8171754647  N,0.1280328866,0.629762756,-2.1370657216  N,0.1579768433,-0.6397871297,-2.1217487279  C,-0.1069416613,2.472265044,-0.5539324987  H,-1.1411203594,2.8077633148,-0.6610035841  H,0.234755652,2.6292387008,0.4692954799  H,0.5265160573,3.0073140552,-1.2613723462  C,0.0391898101,-2.4484713706,-0.4855851805  H,1.055657025,-2.8406124345,-0.563778242  H,-0.3278574892,-2.5536306165,0.5335204872  H,-0.6091463305,-2.9769520687,-1.1854284385</p>
	<p><b>4/OCS (A) NIMAG= 1</b>  C,1.7554648497,2.0133227812,-0.0996249407  S,3.2043836252,1.3583449792,-0.3103085413  O,0.958877764,2.8576611902,0.0139689597  C,0.1611874024,0.2065237182,0.0804243403  C,-1.0809730664,-1.7007487105,0.0162982253  N,-1.93526826,-0.6739584636,-0.0049936227  N,0.1587885266,-1.1946713416,0.0639850181  C,-1.1836585545,0.4973049144,0.0326949787  H,-1.6824788299,1.45332638,0.016855228  H,-1.3595086766,-2.7418824431,-0.0042222993  C,-3.3834919064,-0.7759542311,-0.0771796057  H,-3.6805958072,-1.8255804721,-0.0594412258  H,-3.8369104718,-0.2645947179,0.7757517363  H,-3.7490086098,-0.3183019717,-1.0002801849  C,1.371208437,-1.9989868723,0.1409008217  H,1.6793958466,-2.1265496757,1.1824042469  H,1.2012805393,-2.9802966713,-0.309016388  H,2.1619401919,-1.4729533922,-0.3932167467</p>
	<p><b>4/OCS (B) NIMAG= 1</b>  C,2.5704164696,0.1843698302,0.0320030905  S,2.9604672672,-1.3658644382,0.0667883296  O,2.7235577385,1.3422516754,0.0094944212  C,0.1273241565,0.0961711097,0.0151556754  C,-2.0757955647,0.6785038234,-0.0120635279  N,-2.0196590455,-0.6560185226,0.0167361787  N,-0.8153678528,1.134988412,-0.0132787903  C,-0.6777221161,-1.0214903022,0.0335381238  H,-0.4070668009,-2.0650648601,0.0576323835  H,-2.9825914899,1.261212975,-0.0304667758  C,-3.1638188079,-1.5529100032,0.0281719761  H,-4.0873891303,-0.9724772409,0.0095562188  H,-3.1369428743,-2.2067360049,-0.8473792018  H,-3.1489345181,-2.1687856981,0.9310987496  C,-0.4514478647,2.5471341388,-0.0413093806  H,-0.8321154418,3.0277612277,-0.947298845  H,-0.8500479568,3.0676999292,0.8343785998  H,0.635974632,2.5970213989,-0.0316151756</p>

	<p><b>5/OCS (A) NIMAG= 1</b></p> <p>C,-2.2627774468,-0.5028022618,-0.0390119105  S,-2.0727582603,-2.0986264173,-0.0382448552  O,-2.8416658855,0.5095429807,-0.0465520994  C,-0.0872673074,0.4931397804,-0.0052164982  C,0.0445251198,1.908370751,-0.0021357447  C,1.3832513015,2.2294301959,0.0149001942  N,1.1783470198,0.0479994174,0.0100820097  N,2.103157245,1.0841889119,0.0226758368  C,3.5372481349,0.8982814398,0.0402753214  H,4.0027790408,1.8844971023,0.0479373304  H,3.8586461502,0.3553169913,0.934707441  H,3.8810353717,0.3585942,-0.8478048961  C,1.621564086,-1.3331569182,0.0138776675  H,0.715975328,-1.939477386,0.0011252116  H,2.2242399908,-1.5598841236,-0.8714640834  H,2.2008594709,-1.5625195146,0.9140342946  H,-0.7771216355,2.6071058953,-0.0115953453  H,1.9008072762,3.1774579554,0.0224101256</p>
	<p><b>5/OCS (B) NIMAG= 1</b></p> <p>C,-1.9321857551,-1.1327668087,-0.0484778848  S,-3.1691188718,-0.1173781619,-0.045909063  O,-1.3866562465,-2.1687046785,-0.0585215684  C,-0.0432429557,0.3414641433,-0.0064682906  C,-0.0235696346,1.7620425332,0.0129125941  C,1.2856233941,2.1876222909,0.0335149825  N,1.2549364141,-0.0021638957,0.0040285986  N,2.0949184638,1.1033106449,0.0276377155  C,3.5391760407,1.0317282234,0.0493385743  H,3.9252014196,2.0516651264,0.0626629474  H,3.9001593392,0.5117490286,0.9424452146  H,3.927086875,0.5250702202,-0.8400170593  C,1.8047376069,-1.3450781356,-0.0099728502  H,0.9504604026,-2.0199808075,-0.027248344  H,2.4205846633,-1.5131309698,-0.8994364471  H,2.4045407738,-1.5384092827,0.8852818925  H,-0.8985084093,2.3929295436,0.0111583487  H,1.7257004797,3.1738299857,0.0520706392</p>
	<p><b>6/OCS (A) NIMAG= 1</b></p> <p>C,-2.8239490853,-0.770427018,-0.0692274519  S,-3.6561301848,0.6114938448,-0.0790334019  O,-2.7191478835,-1.9365095506,-0.0742033995  C,-0.5958118595,-0.2866700954,-0.0216588722  N,1.5329475844,0.5642408162,0.0213986811  N,1.5837957293,-0.7521541719,0.0028655981  N,0.2217854199,0.8081920955,0.0059671433  C,0.3432421769,-1.3099713794,-0.0238933071  H,0.2107555187,-2.3795391798,-0.0407040328  C,2.8823416796,-1.4098234708,-0.0131565248  H,3.6441045374,-0.6621555683,0.2021209842  H,2.9019999531,-2.1918881291,0.7480674063  H,3.065915693,-1.8526622916,-0.9950408655  C,-0.2143756555,2.1996584482,0.0280422397  H,0.1291862061,2.6816706314,0.9458134996  H,0.1952706072,2.7295260913,-0.8343445151  H,-1.3029337071,2.1916445173,-0.0112943716</p>

	<p>6/OCS (B) NIMAG= 1</p> <p>C,-2.51819954,-0.4867237736,-0.1264933167  S,-2.6674387475,-2.0860363125,-0.2150597375  O,-2.9163737706,0.6144732691,-0.0809419567  C,-0.2374597093,-0.1583173169,-0.0391089607  N,1.8117921668,0.8702439811,0.0707133267  N,1.9742654605,-0.4361436722,0.0085942798  N,0.4847211887,1.0008158882,0.0402566649  C,0.7865819748,-1.0963461758,-0.0576889707  H,0.7456461724,-2.171936517,-0.1147008475  C,3.3225987903,-0.9839122446,0.0397309812  H,4.025876224,-0.1596186551,-0.0676899764  H,3.4960259992,-1.4971974441,0.9885452265  H,3.4471051784,-1.6897440081,-0.7836322135  C,-0.0728155451,2.3477641719,0.0878253369  H,0.23522824,2.8448858737,1.0101174988  H,0.2796465947,2.9263588804,-0.7687461698  H,-1.155735677,2.2436470553,0.0556618348</p>
	<p>7/OCS NIMAG= 1</p> <p>C,-0.0000009106,0.1437984606,3.1549181612  S,0.0000855014,1.7377486295,3.2731292673  O,-0.0000626425,-0.9799608444,3.4518601702  C,-0.0000115928,-0.1515467739,0.6314626946  C,0.0000507294,0.9618865401,-0.2060847852  C,-0.0000657331,-1.1839816031,-0.3044026939  N,0.0000354435,0.6289090837,-1.5289713158  N,-0.0000382252,-0.7285664031,-1.5937123593  C,-0.0000751122,-1.4560263268,-2.8448506345  H,-0.0001333739,-2.5178726517,-2.5967276918  H,-0.8927988303,-1.2378022098,-3.439996349  H,0.8926748663,-1.2378992869,-3.4399925453  C,0.0000837182,1.4706621282,-2.7063352329  H,0.0001391832,2.5043797044,-2.3595506695  H,0.8927716048,1.3084173556,-3.3189998527  H,-0.8926191954,1.3085144282,-3.3190036563  H,0.0001075706,2.0170361521,0.0416805886  H,-0.0001244902,-2.2594195175,-0.1706014201</p>

**Table S3.** Dihedral angles (°) for the different NHC-CXY products.

NHC	NHC-CO <sub>2</sub>	NHC-OCS	NHC-CS <sub>2</sub>
<b>1</b>	17	54	82
<b>2</b>	0	53	85
<b>3</b>	0	53	81
<b>4</b>	0	0	55
<b>5</b>	0	19	86
<b>6</b>	0	10	56
<b>7</b>	0	0	0



**Table S4.** Chemical bonding analysis (EDA-ADF) for non-covalent complexes. For the OCS complexes, the most stable complexes are shown.

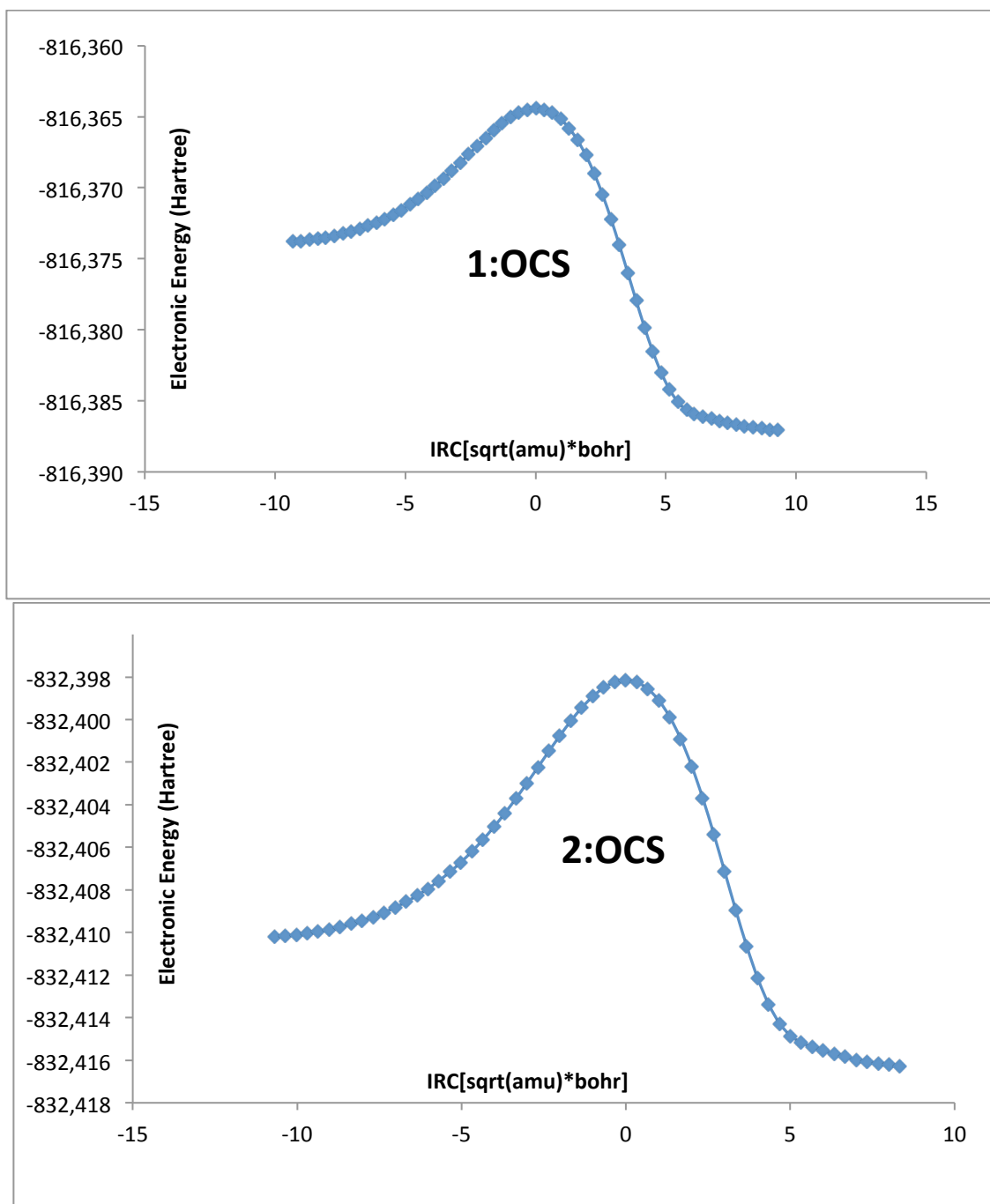
	1:CS2	2:CS2	3:CS2	4:CS2	5:CS2	6:CS2	7:CS2
Electrostatic E.	-16.9	-14.6	-12.00	-23.72	-20.72	-19.34	-27.55
Kinetic E.	-434.28	-495.14	-525.09	-439.6	-453.55	-459.5	-438.37
Steric+OI E.	419.1	475.37	500.68	434.39	442.03	447.57	436.57
XC E.	26.91	30.22	33.46	20	24.57	24.53	18.39
Total B. E.	-5.17	-4.16	-2.95	-8.94	-7.68	-6.74	-10.97

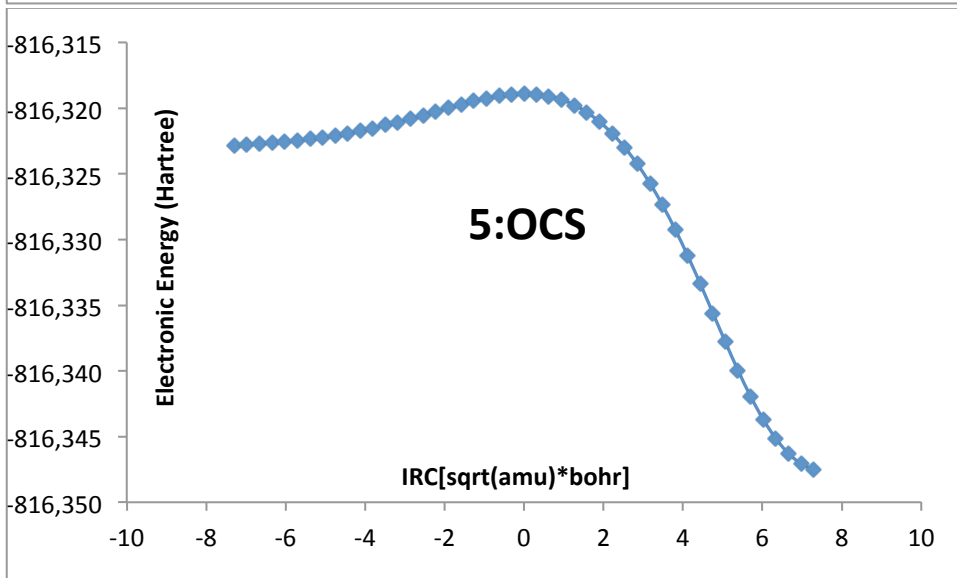
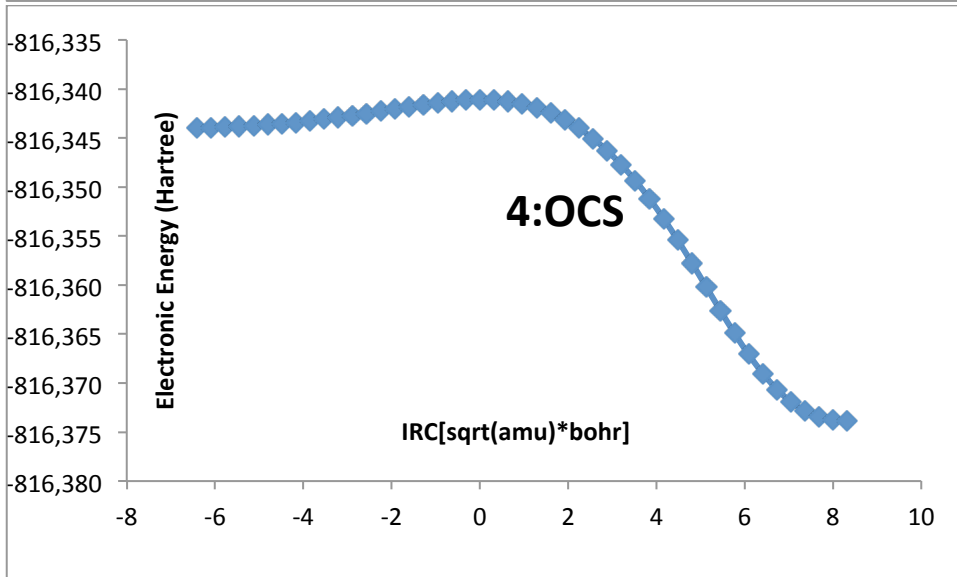
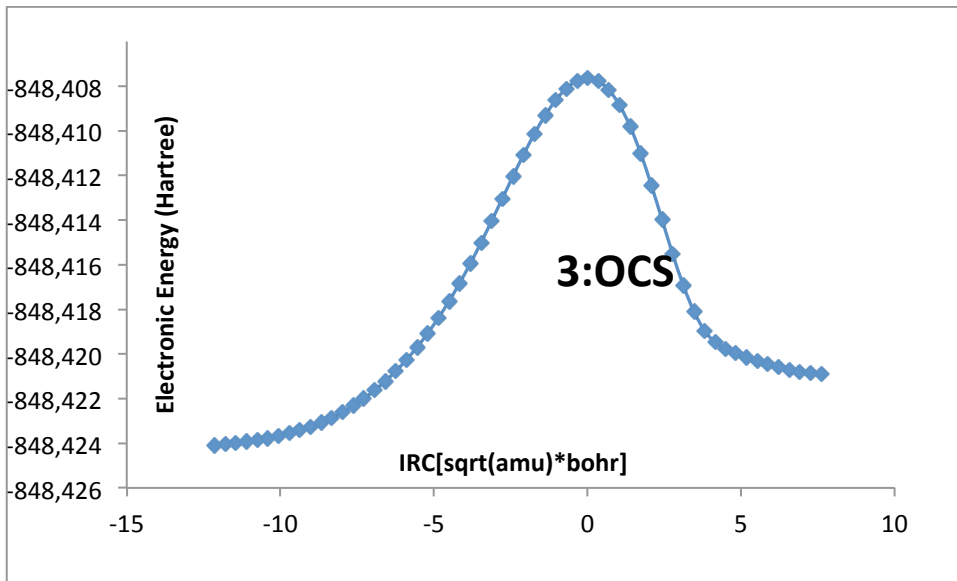
	1:CO2	2:CO2	3:CO2	4:CO2	5:CO2	6:CO2	7:CO2
Electrostatic E.	-44.78	-39.32	-33.48	-59.13	-54.33	-45.92	-66.17
Kinetic E.	-38.46	-90.64	-115.02	-53.99	-62.74	-75.44	-45.53
Steric+OI E.	92.34	135.7	151.13	127.63	127.28	128.41	128.47
XC E.	-21.91	-16.63	-11.36	-33.79	-27.89	-21.51	-40.44
Total B. E.	-12.81	-10.88	-8.74	-19.28	-17.68	-14.46	-23.66

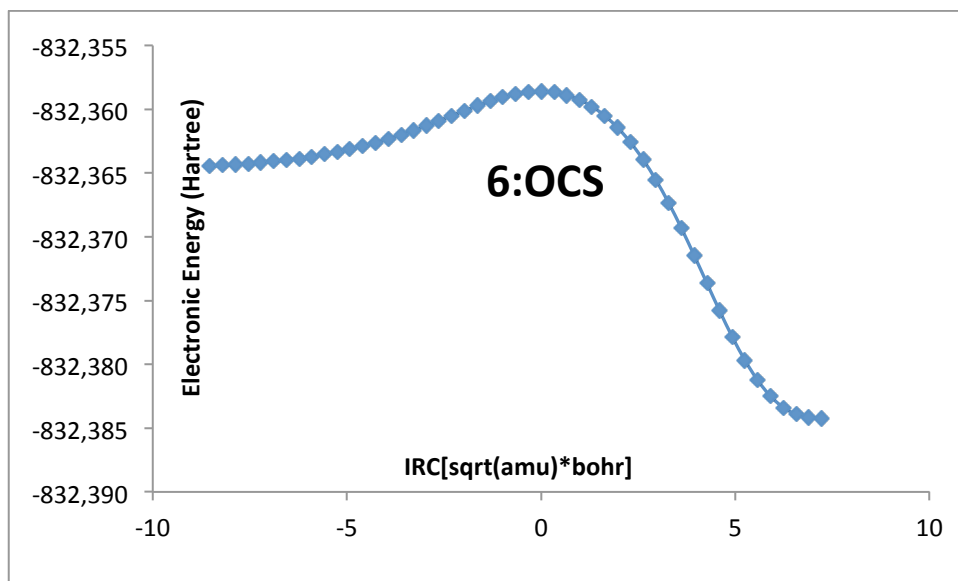
	1:OCS	2:OCS	3:OCS	4:OCS	5:OCS	6:OCS	7:OCS
Electrostatic E.	-21.83	-18.8	-15.44	-29.75	-26.52	-24.56	-34.41
Kinetic E.	-315.06	-380.62	-414.62	-307.29	-331.13	-337.62	-302.66
Steric+OI E.	322.65	381.39	408.53	329.94	345.17	349.94	330.84
XC E.	6.45	11.59	16.68	-4.95	1.84	2.77	-8.11
Total B. E.	-7.79	-6.43	-4.85	-12.05	-10.65	-9.48	-14.34

**Figure S1.** Intrinsic Reaction Path (IRC) calculations for several NHC + CXY reactions.

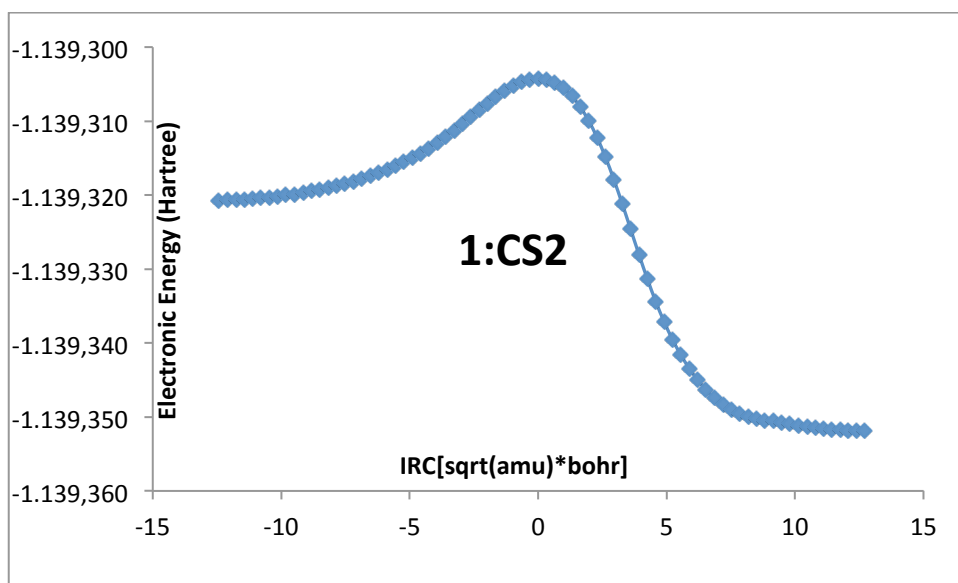
**(A)** IRC coordinates vs. the total electronic energies for reactions **1-6** + OCS. The geometries on the most negative value of the IRC corresponds to the NHC:OCS complex while the most positive one corresponds to the NHC-OCS molecule.

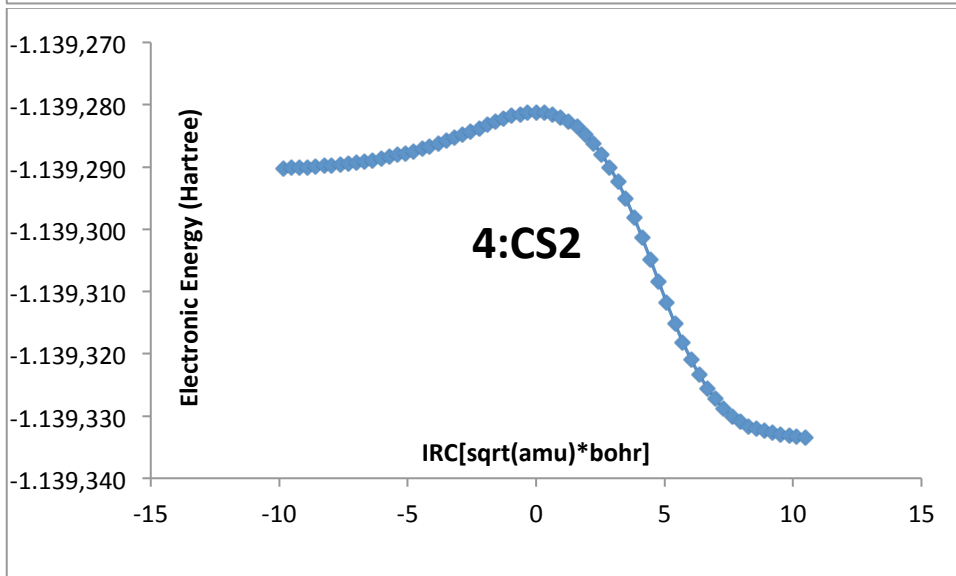
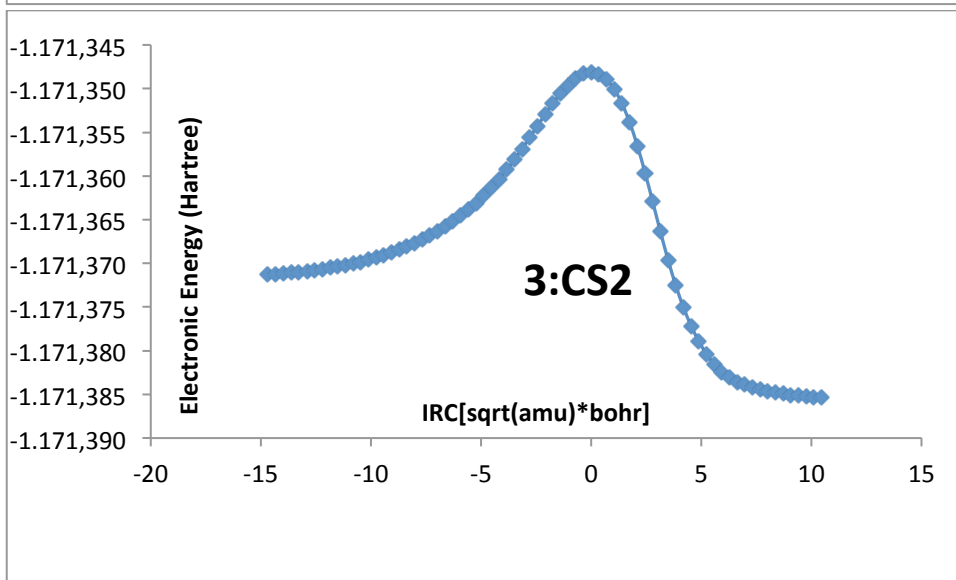
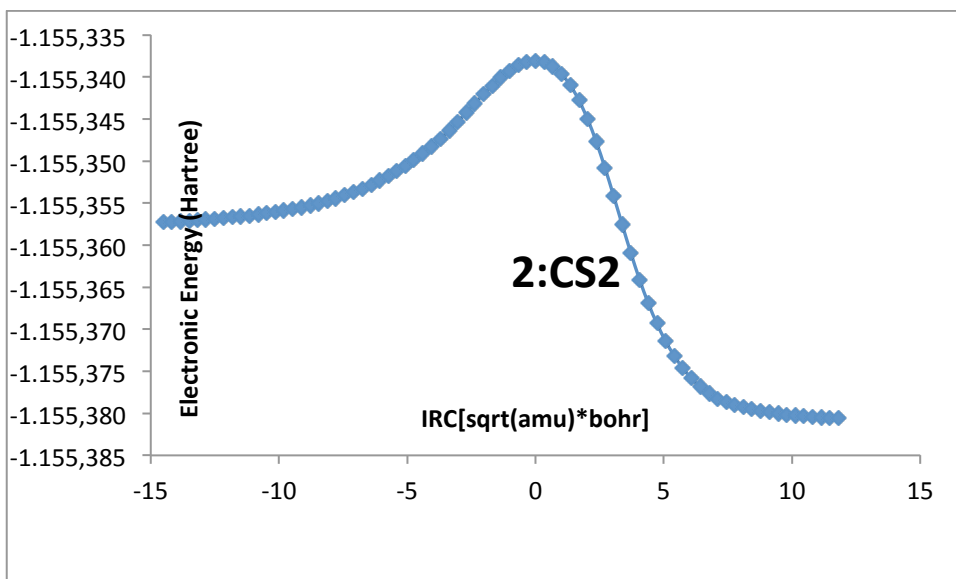


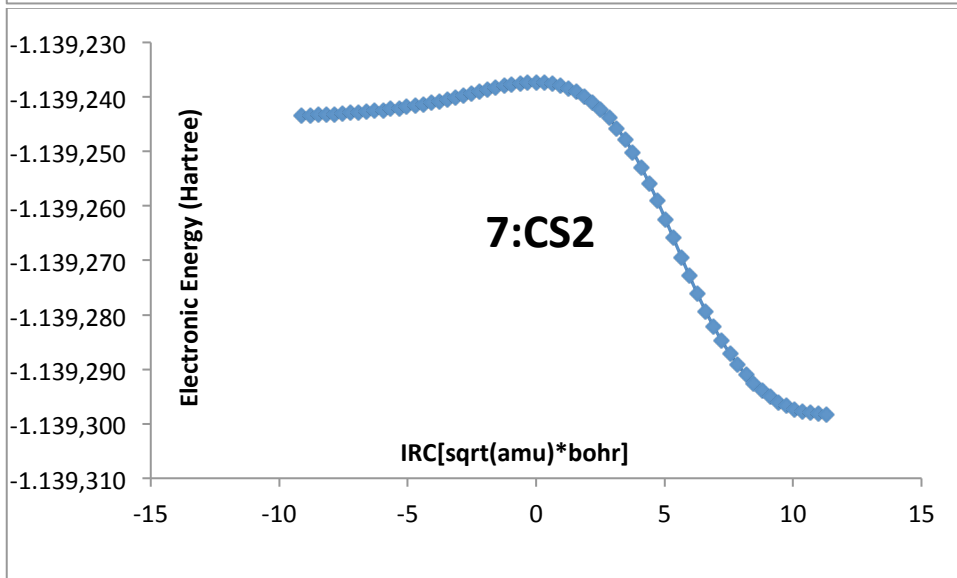
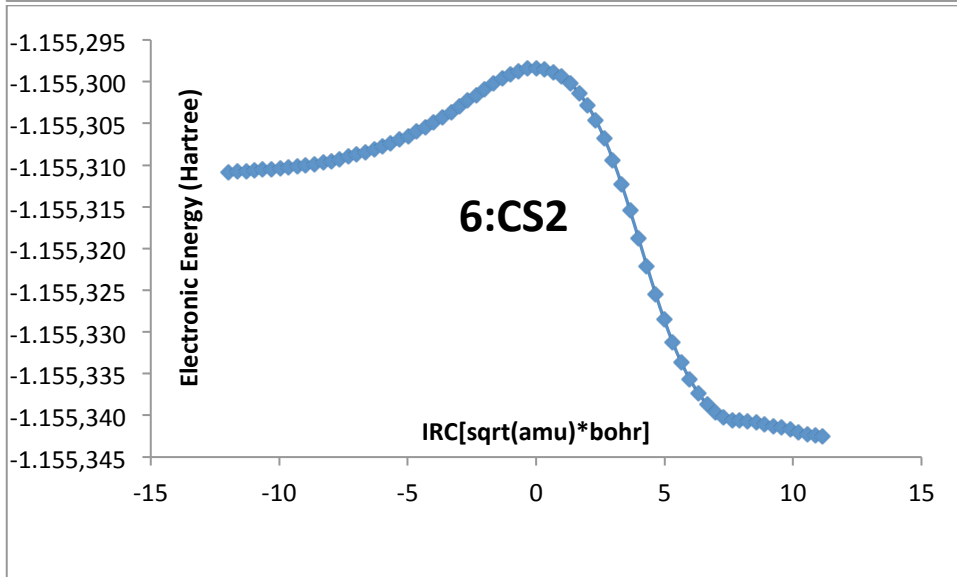
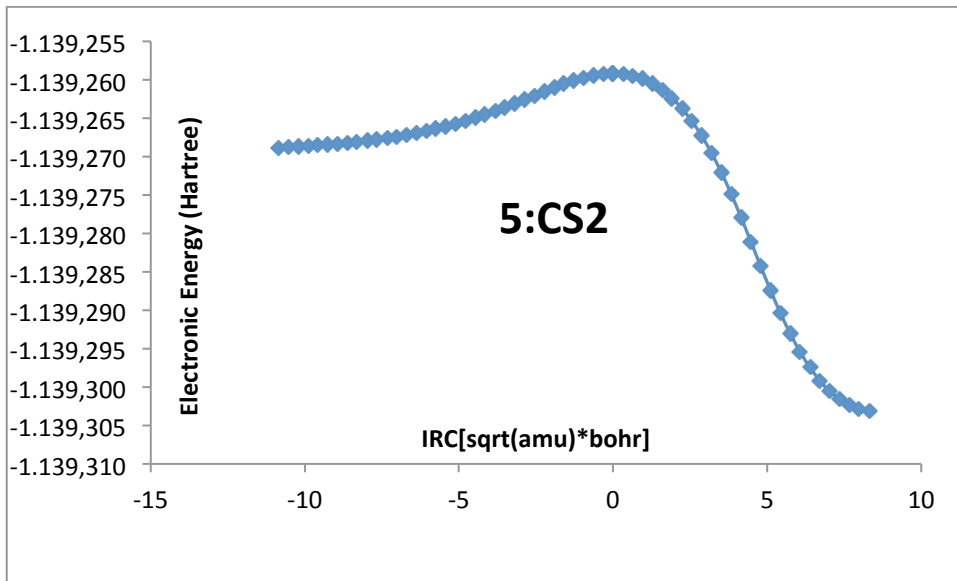




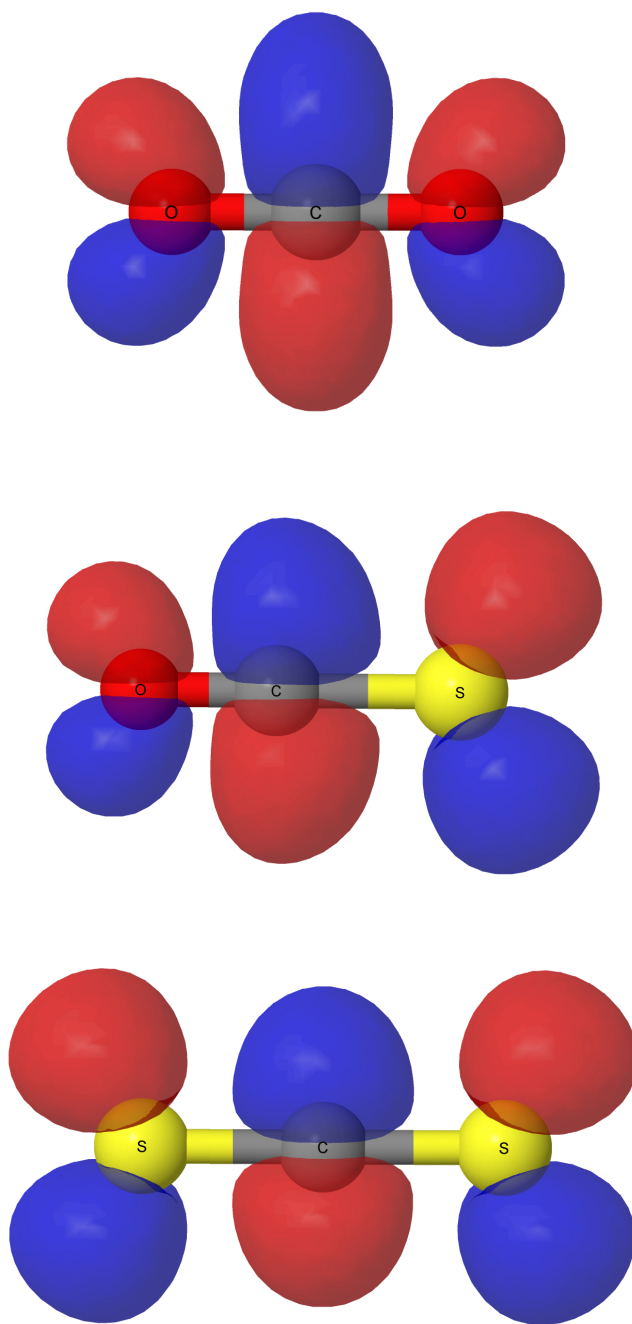
(B) IRC coordinates vs. the total electronic energies for reactions **1-7** + CS<sub>2</sub>. The geometries on the most negative value of the IRC corresponds to the NHC:CS<sub>2</sub> complex while the most positive one corresponds to the NHC-CS<sub>2</sub> molecule.



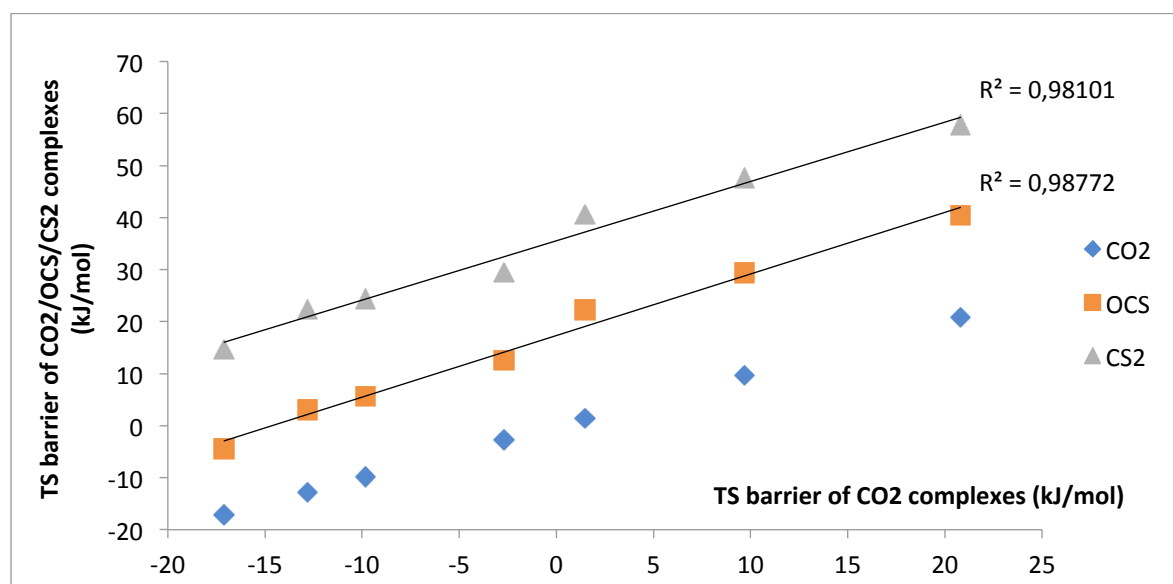




**Figure S2.** CO<sub>2</sub>, OCS and CS<sub>2</sub> LUMO orbitals.

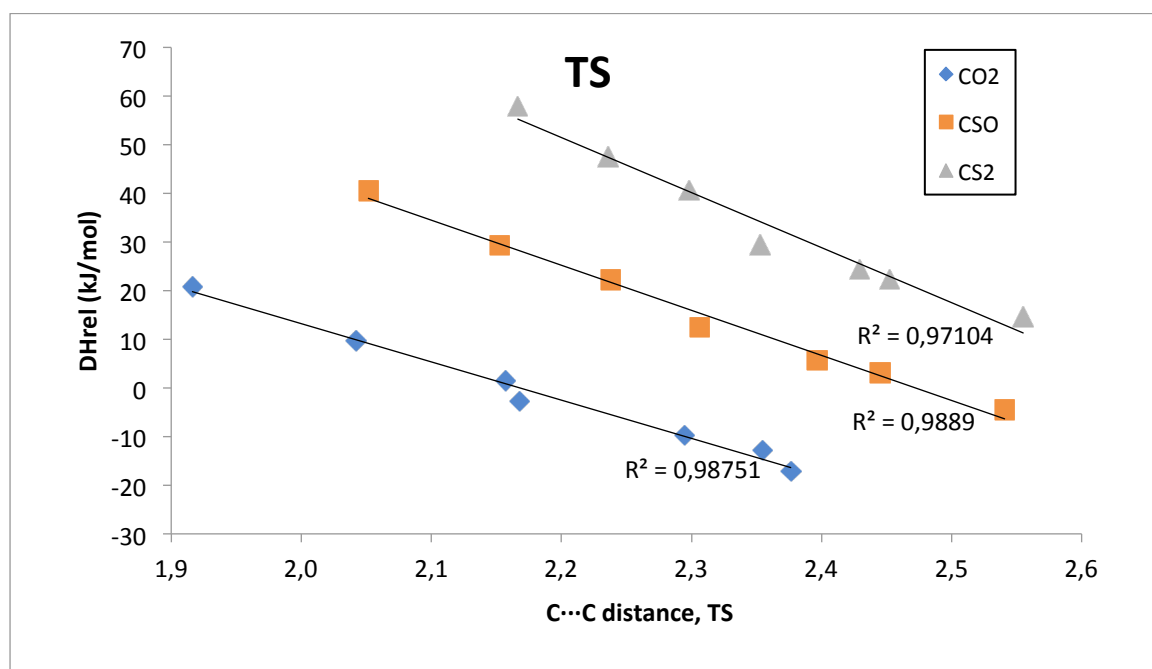


**Figure S3.** Stability of the TSs NHC/CXY (NHC=1-7, CXY = CS<sub>2</sub>, OCS) versus the stability of the TSs NHC/CO<sub>2</sub>.



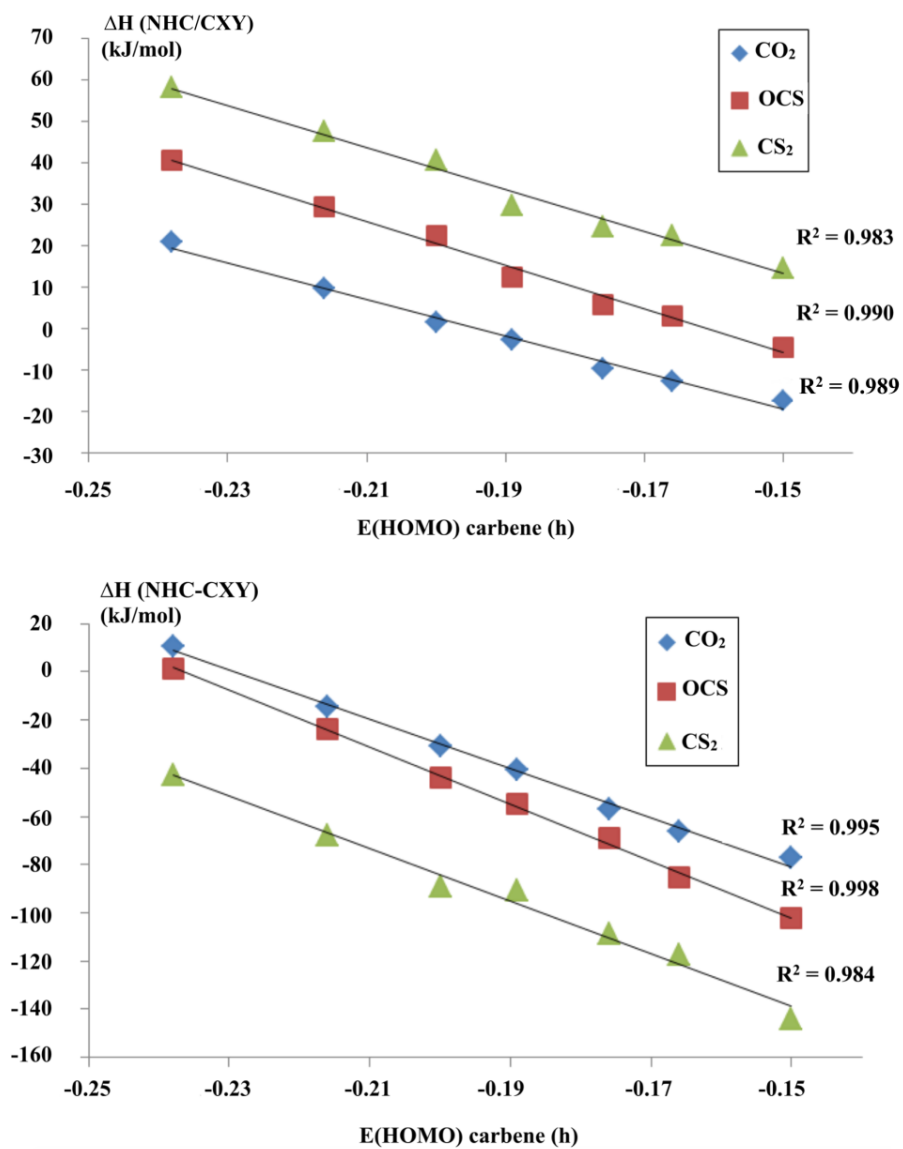


**Figure S4.** Stability of the TSs (kJ/mol) NHC/CXY (NHC=1-7, CXY = CO<sub>2</sub>, CS<sub>2</sub>, OCS) versus C···C distances (Å).

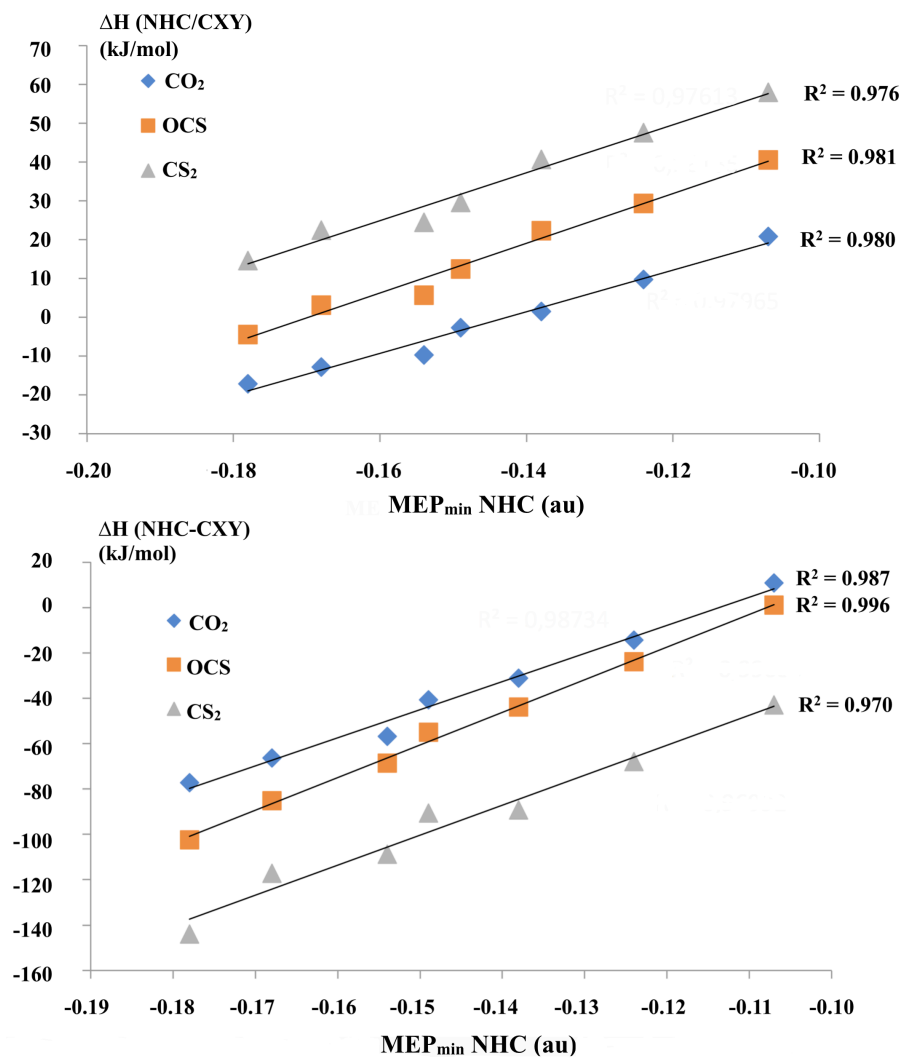


Linear correlations: TS(CO<sub>2</sub>) vs TS(OCS), R<sup>2</sup> = 0.988; TS(CO<sub>2</sub>) vs TS(CS<sub>2</sub>), R<sup>2</sup> = 0.981; TS(OCS) vs. TS(CS<sub>2</sub>), R<sup>2</sup> = 0.998.

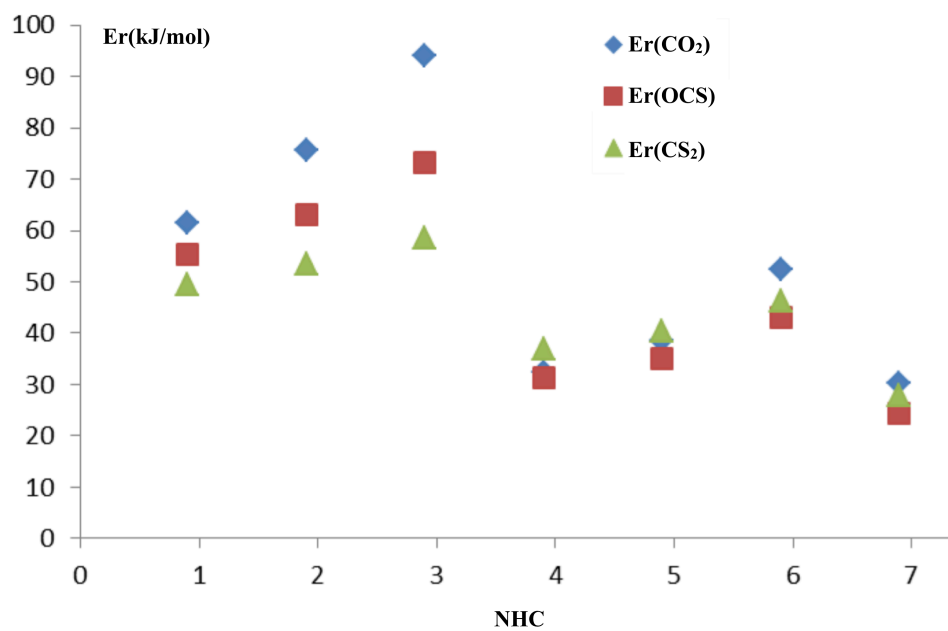
**Figure S5.** Relationship between the  $\Delta H$  of the transition states NHC/CXY and products NHC-CXY (NHC = **1-7**, CXY = CO<sub>2</sub>, OCS, CS<sub>2</sub>) with respect to the energy of the HOMO in the isolated **1-7** carbenes. Results regarding CO<sub>2</sub> were taken from Ref. 3.



**Figure S6.** Relationship between the  $\Delta H$  of the transition states NHC/CXY and products NHC-CXY (NHC = **1-7**, CXY = CO<sub>2</sub>, OCS, CS<sub>2</sub>) with respect to the minimum of the MEP in the isolated **1-7** carbenes.

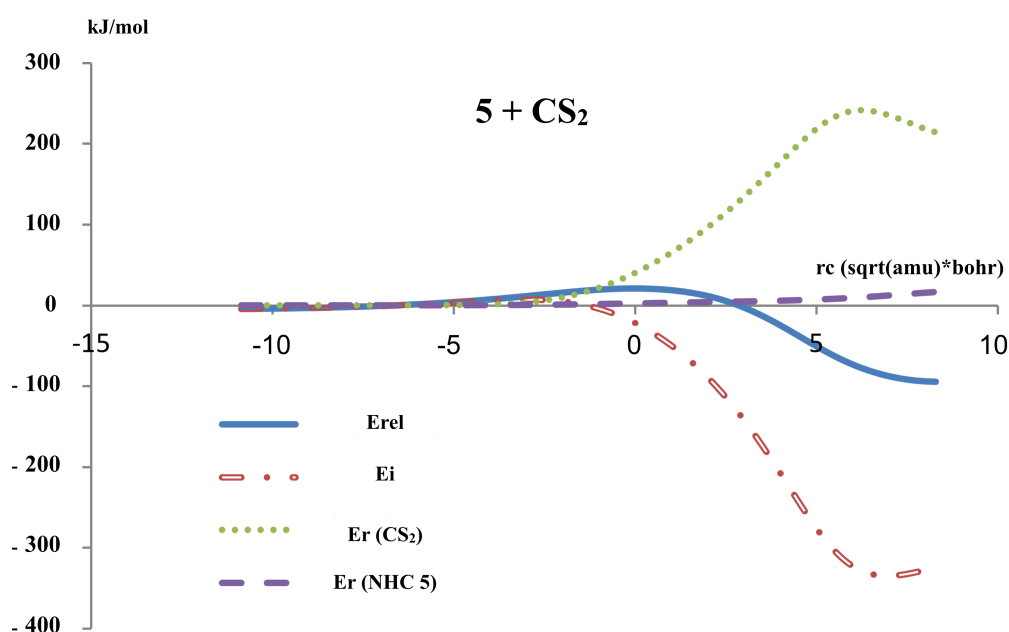


**Figure S7.**  $E_r$  (distortion energy) for the different CXY molecules at the NHC/CXY transition states from the distortion-interaction analysis.



**Figure S8.** Distortion-interaction analysis carried out along the path of the NHC + CXY reactions. Negative and positive values of the IRC correspond to the complexes and adducts, respectively.

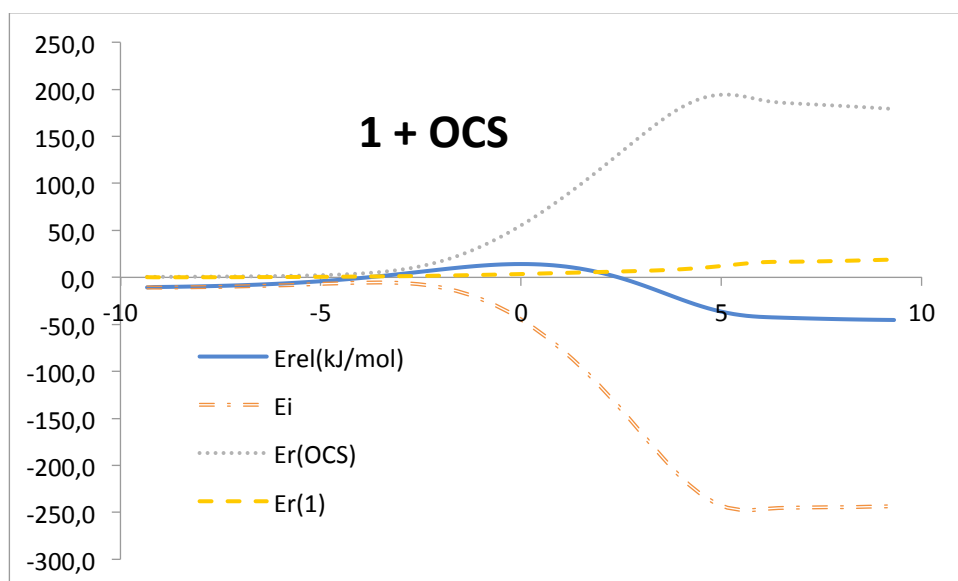
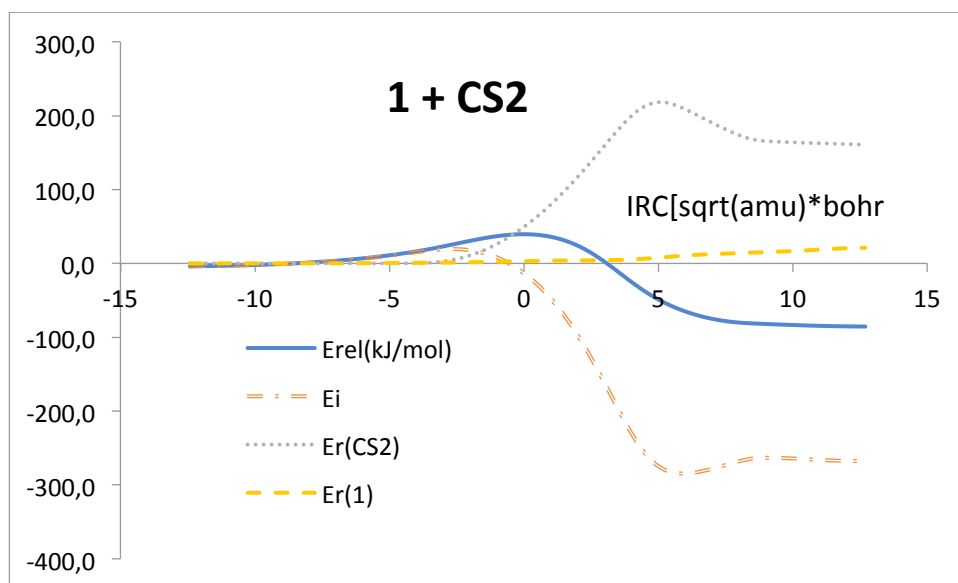
Starting from the paths explored with the help of the IRC calculations, we also carried out this distortion-interaction analysis for some selected cases all along the reaction paths. In particular, Figure S6.1 below these lines describes the trends of the different energy terms involved for the **5** + CS<sub>2</sub> reaction, which presents the highest interaction energy at the TS of the CS<sub>2</sub> group of reactions.

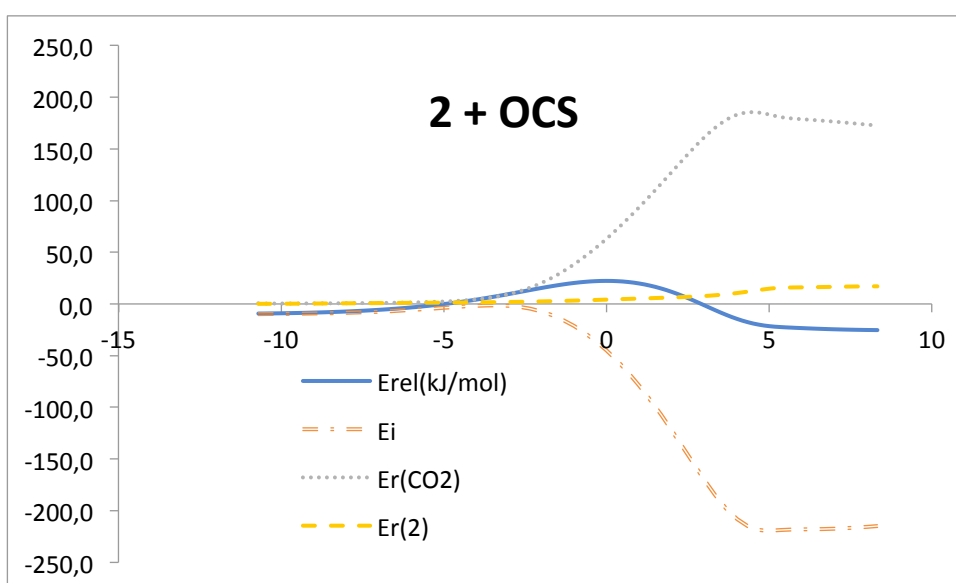
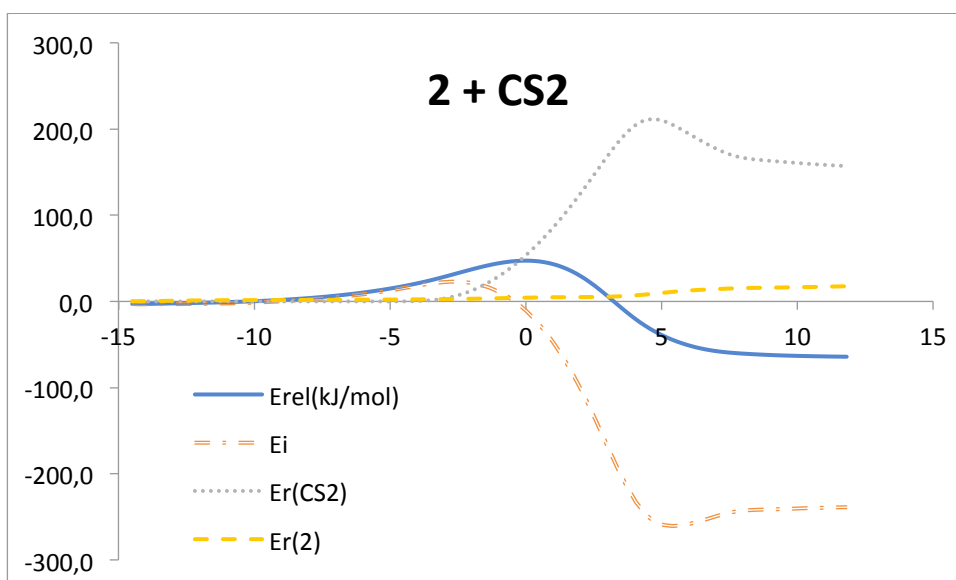
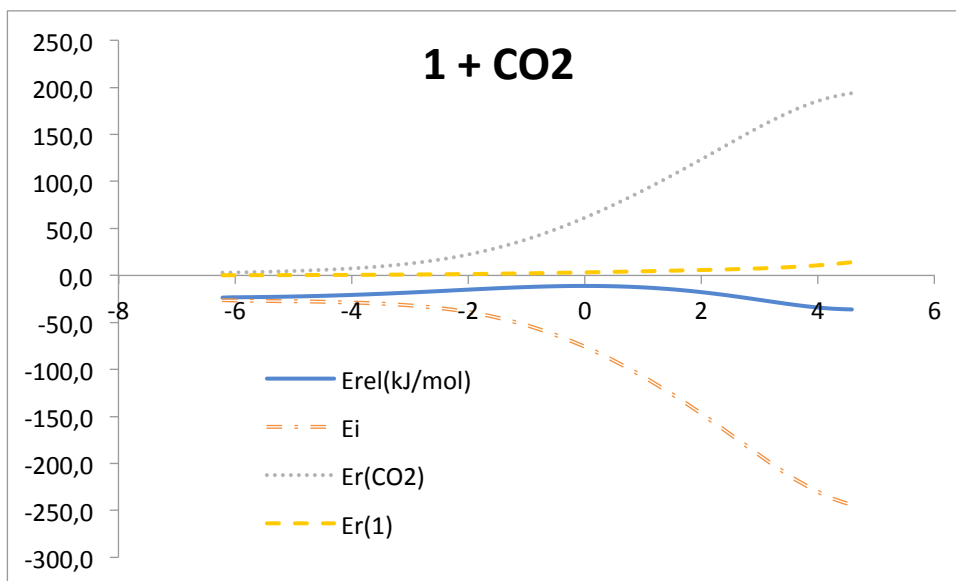


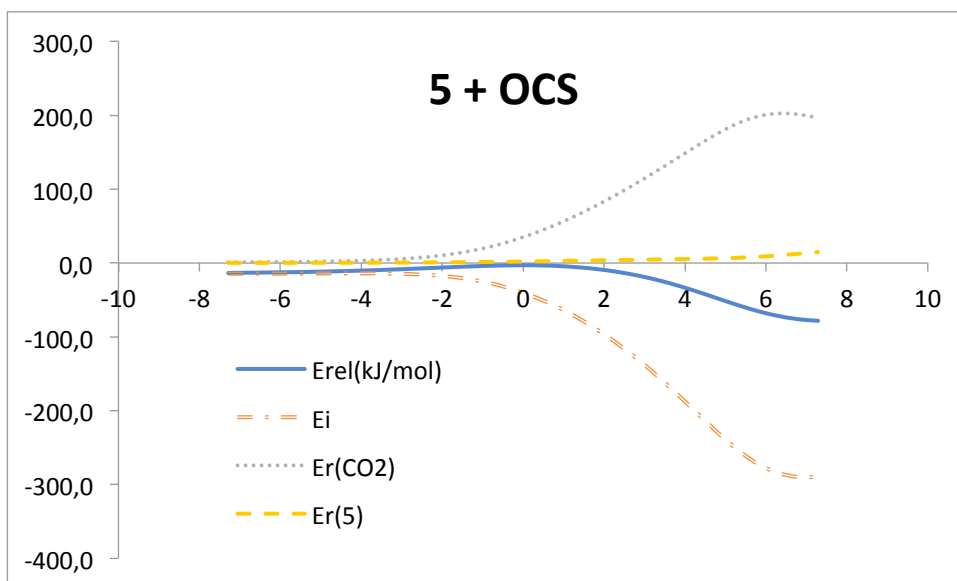
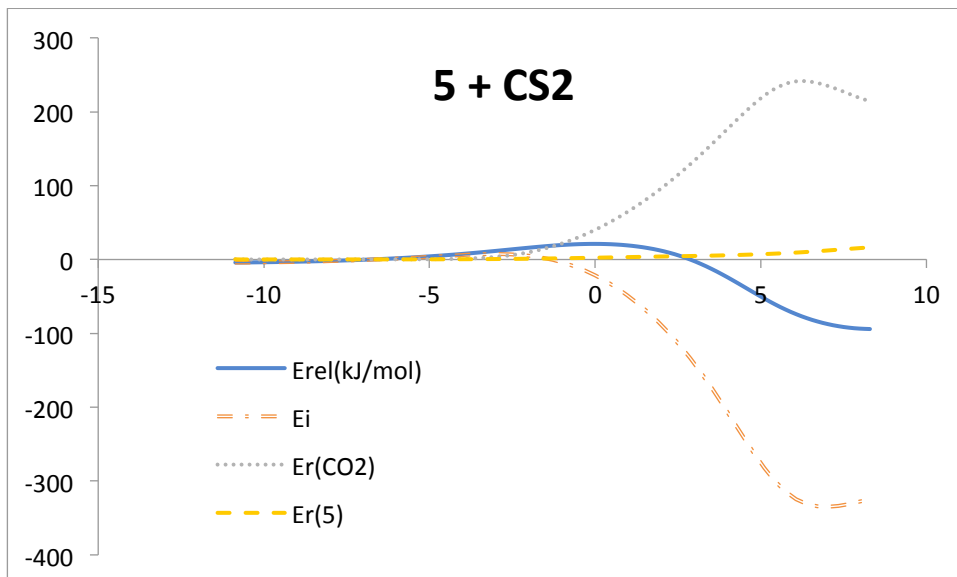
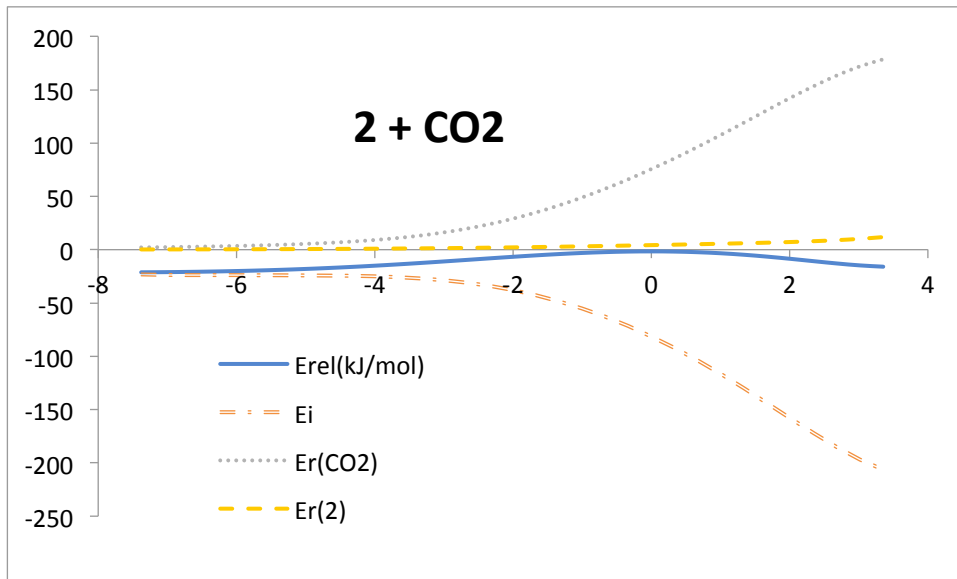
**Figure S6.1** Distortion-interaction analysis carried out along the path of the reaction between the NHC **5** and CS<sub>2</sub>. Notations  $E_{rel}$ ,  $E_i$  and  $E_r$  stand for the total relative energy, the interaction energy and the distortion (repulsive) energy, respectively (kJ/mol).

The energy terms are contained in a narrow interval of energy values before the TS; after that point, they dramatically change as an indication of the formation of the new C-C bond, reaching very large values at the product (positive in the case of the distortion terms, and negative in the case of the interaction energy). Two interesting things come out from the picture: (i) the highest point of the interaction energy is not the TS, (ii) the highest point of the deformation energy for the CS<sub>2</sub> is not the product. This latter point does not apply for the CO<sub>2</sub> case, which continues gaining distortion energy until the final product is reached. The maximum value of the deformation energy of the CS<sub>2</sub> is closed to where the largest C-S bond distance and shortest SCS angles are found along the reaction coordinate. A similar

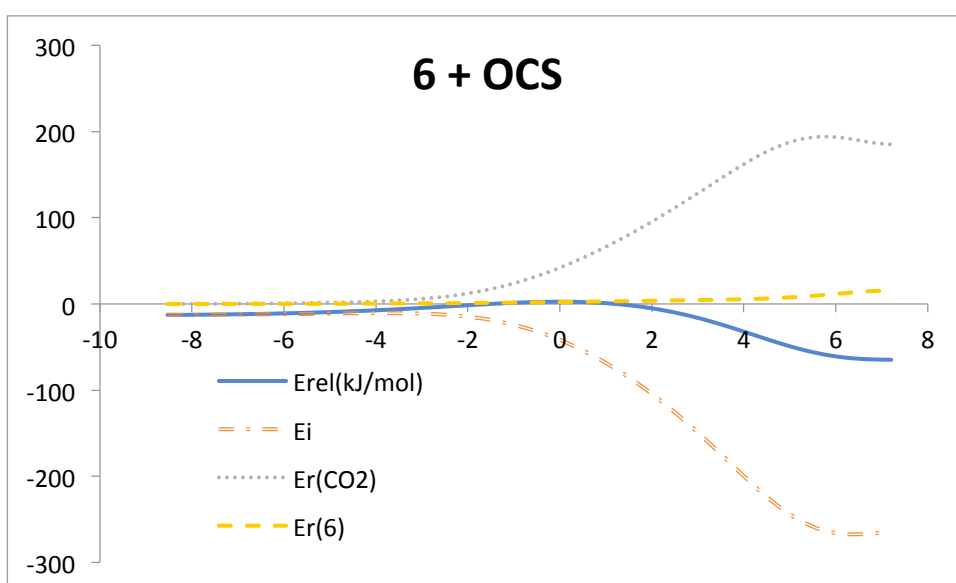
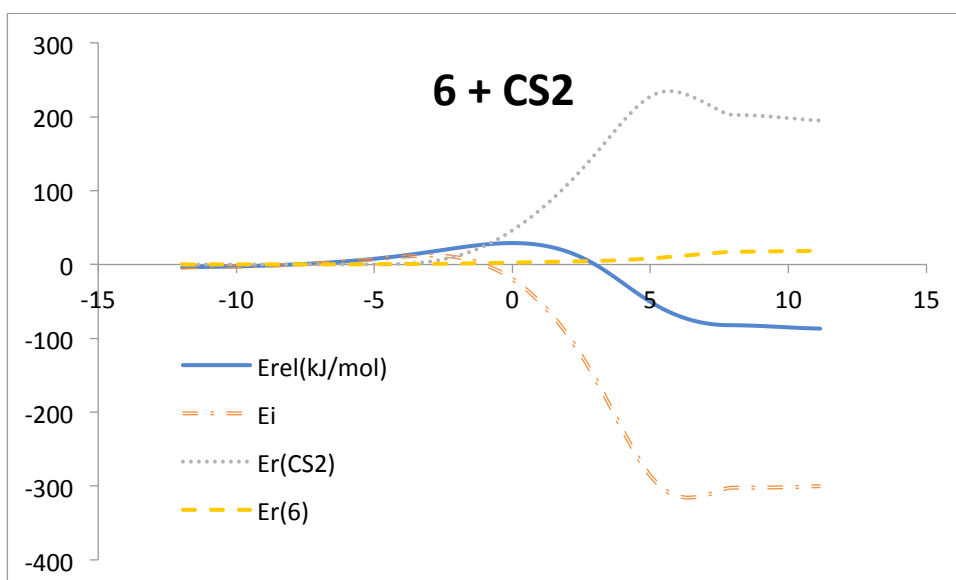
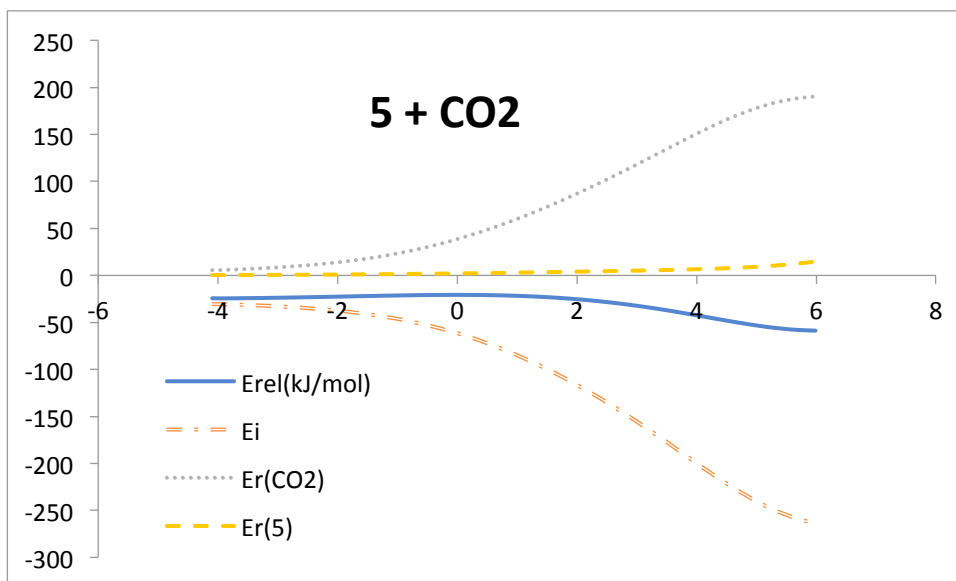
behaviour is found for some of the NHC + CS<sub>2</sub> and OCS reactions studied for which the complete IRC was obtained (Figures S6.2):

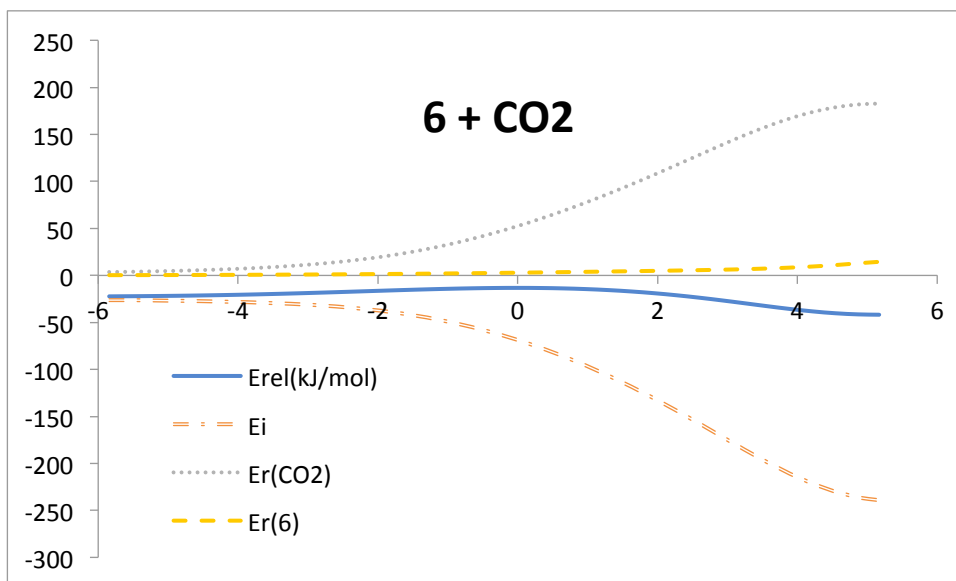












Figures **S6.2**. Distortion-interaction analysis carried out along the path of the reaction between some NHCs and OCS/CS<sub>2</sub>. Notations E<sub>rel</sub>, E<sub>i</sub> and E<sub>r</sub> stand for the total relative energy, the interaction energy and the distortion (repulsive) energy, respectively (kJ/mol).