

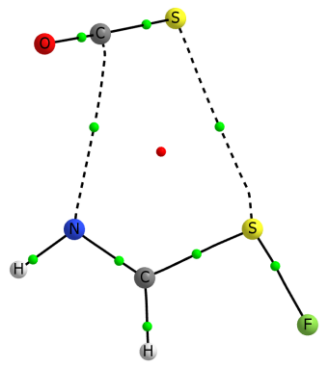
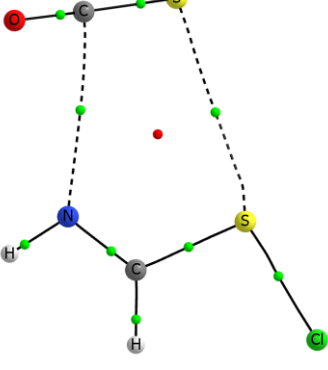
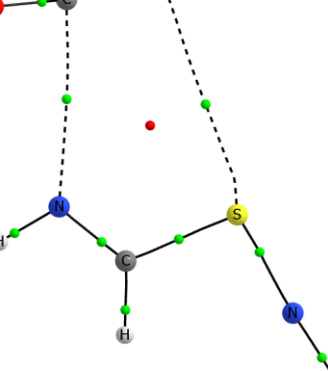
## Supporting Information for

### N $\cdots$ C and S $\cdots$ S Interactions in Complexes, Molecules, and Transition Structures HN(CH)SX:SCO, for X = F, Cl, NC, CCH, H, and CN

Janet E. Del Bene,<sup>a,\*</sup> Ibon Alkorta,<sup>b,\*</sup> José Elguero<sup>b</sup>

Pgs. S2-S3:	Table S1. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO complexes with C <sub>1</sub> symmetry
Pgs. S4-S5:	Table S2. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO complexes with C <sub>s</sub> symmetry
Pgs. S6-S7:	Table S3. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO molecules
Pgs. S8-S9:	Table S4. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO transition structures
Pg. S10:	Table S5. PSO, DSO, FC, and SD components of <sup>1</sup> tJ(N-C) and <sup>1</sup> cJ(S-S) for complexes, bound molecules, and transition structures with C <sub>s</sub> symmetry

Table S1. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO complexes with  $C_1$  symmetry

	<p>hnchsf_sco_complex  MP2= -1102.18853592 NIM= 0  C,-0.6737495662,-2.2012722223,0.1645530725  O,0.0532609366,-2.9268096337,0.7169785976  S,-1.6766472384,-1.2436895447,-0.5714897163  N,1.6918437011,-0.4329296105,-0.3938703477  C,1.560761095,0.8154417164,-0.1761502041  S,-0.0118818309,1.5304951395,0.1266985267  F,0.5368481926,3.0523713662,0.3768651143  H,2.3488139606,1.5723381045,-0.1463712087  H,2.6733607497,-0.6558383154,-0.5522138342</p>
	<p>hnchsc1_sco_complex  MP2= -1462.18814858 NIM= 0  C,-0.6923592381,-2.2915930954,0.1533796536  O,0.0737255525,-2.9619502662,0.7243677845  S,-1.7412821452,-1.4070577005,-0.6065270613  N,1.6780357802,-0.4379893331,-0.3952330875  C,1.5873541237,0.8123939283,-0.1800105286  S,-0.0101869908,1.5095375729,0.1114305684  Cl,0.5607083959,3.4382425066,0.4376474273  H,2.3950202421,1.5463124995,-0.1495910041  H,2.6515942799,-0.6977891119,-0.5504637522</p>
	<p>hnchsn1_sco_complex  MP2= -1095.10126112 NIM= 0  C,-0.7005348145,-2.3694582265,0.0511743103  O,0.1152278371,-3.1733114488,0.2738593347  S,-1.816932929,-1.3081469626,-0.2469797248  N,1.6511863137,-0.4221899418,-0.1987426584  C,1.6149827897,0.8425103602,-0.1055645497  S,0.0473990238,1.6186707028,0.191208042  N,0.6066224733,3.1842652828,0.2630250685  H,2.4383166599,1.5547617205,-0.1846916768  H,2.6044911887,-0.7393999663,-0.3720943088  C,0.9418514574,4.3224054797,0.3238061631</p>

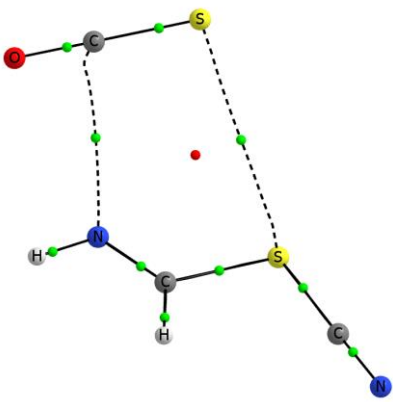
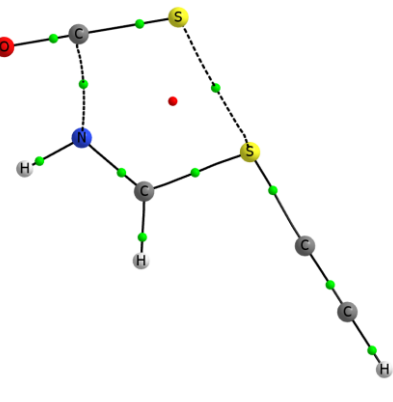
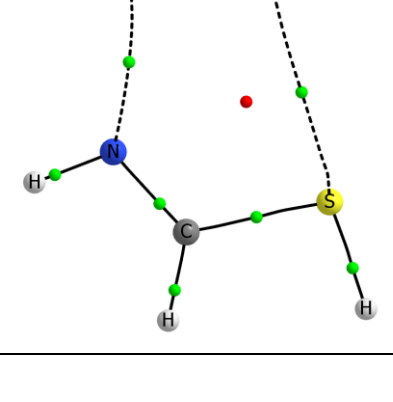
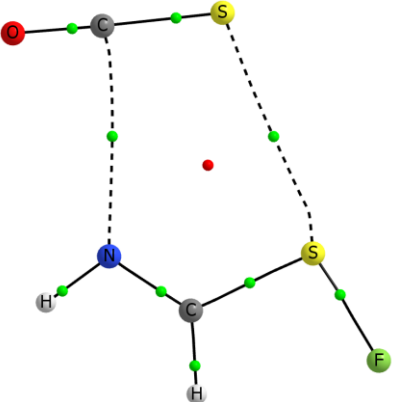
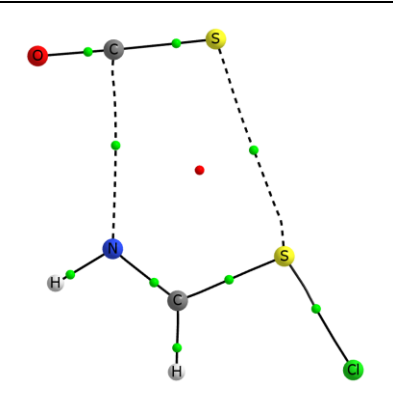
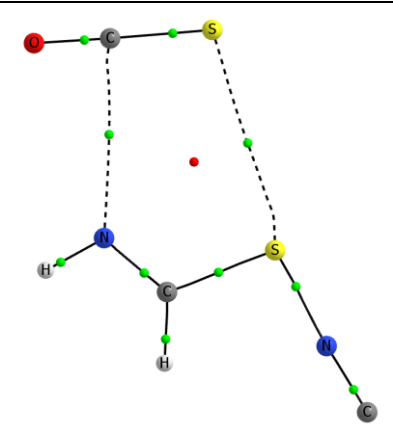
	<p>hnhcscn:sco cis  MP2/aug'-cc-pVTZ= -1095.15217600 NIM= 0  C,2.4199929934,0.1969289269,0.4568714623  O,2.8603698776,1.2799265172,0.4884904382  S,1.8324594079,-1.2540436015,0.4290613475  N,0.144804519,1.6174971991,-0.9769258203  C,-0.9724404353,1.2212324885,-0.5268584171  S,-1.5449181791,-0.3756103009,-1.070868781  C,-3.0034598136,-0.3909863304,-0.2102787847  H,-1.6442847732,1.7321392253,0.1634327174  H,0.3775133739,2.5370080082,-0.60115141  N,-4.0199054856,-0.4198807296,0.3815658843</p>
	<p>hnhscch_sco_complex  MP2= -1079.05835662 NIM= 0  C,2.4226930363,0.2019940394,0.4582025033  O,2.8939687854,1.2722932309,0.4866111315  S,1.7957537097,-1.2321141238,0.4357598273  N,0.1625669426,1.6242259562,-0.9810356403  C,-0.9600100278,1.2219914518,-0.5392486697  S,-1.5576315051,-0.3566654326,-1.077349409  C,-3.0060548403,-0.3959680368,-0.2084111488  H,-1.6279974044,1.7364065759,0.153460286  H,0.3867981071,2.5411537906,-0.5943407163  C,-4.0599553185,-0.4691060487,0.3996904726  H,-4.9790334849,-0.5330784029,0.9296943634</p>
	<p>hnhcsh_sco_complex  MP2= -1003.07649272 NIM= 0  C,1.8401868177,0.4048395797,0.2528756209  O,2.1563399266,1.5148450983,0.0644995737  S,1.4337424868,-1.0839670627,0.5161671165  N,-0.8023316074,1.2917375902,-0.8981857995  C,-1.8470145358,0.8158146162,-0.3419338303  S,-2.221844445,-0.8899930558,-0.5384795195  H,-3.3488713611,-0.8526838351,0.1801621361  H,-2.55393354,1.3792434868,0.2675654599  H,-0.7187327417,2.2867165823,-0.6910147578</p>

Table S2. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO complexes with  $C_s$  symmetry

	<p>hnchsf_sco_complex  MP2= -1102.18845511 NIM= 1  C,1.9199943898,-0.611200373,0.  O,2.7901716149,0.165112193,0.  S,0.7763398217,-1.6866408715,0.  N,0.0484660751,1.7389333927,0.  C,-1.2234788261,1.6671397561,0.  S,-2.0436047254,0.1183862475,0.  F,-3.5642190488,0.7224074973,0.  H,-1.9382137244,2.4941736145,0.  H,0.3418534232,2.7146735433,0.</p>
	<p>hnchsc1_sco_complex  MP2= -1462.18813028 NIM= 1  C,-0.0411475472,-2.8511648733,0.  O,0.9641324133,-3.4439750339,0.  S,-1.4083573103,-2.0825083712,0.  N,1.7319688777,-0.3678079423,0.  C,1.3805519378,0.8546096287,0.  S,-0.3433334243,1.2396187936,0.  Cl,-0.1986435192,3.2716152358,0.  H,2.0244835791,1.7362810425,0.  H,2.7487241231,-0.4423339499,0.</p>
	<p>hnchsn1_sco_complex  MP2= -1095.10125561 NIM= 1  C,2.7909659225,0.0351406968,0.  O,3.3326268544,1.0685203331,0.  S,2.089021074,-1.367932566,0.  N,0.2274102038,1.7057841401,0.  C,-0.9786362191,1.3123531886,0.  S,-1.2923577592,-0.4337191999,0.  N,-2.9537375014,-0.3419887779,0.  H,-1.8905217838,1.9123274895,0.  H,0.2702664322,2.7244027264,0.  C,-4.1417541084,-0.3445680625,0.</p>

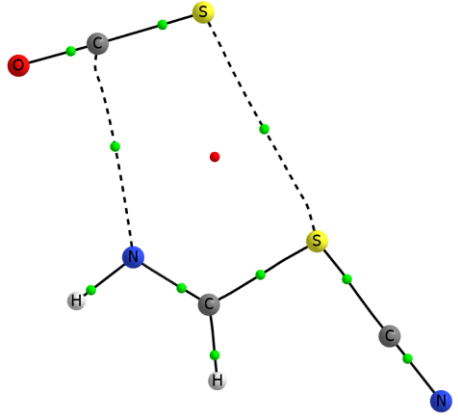
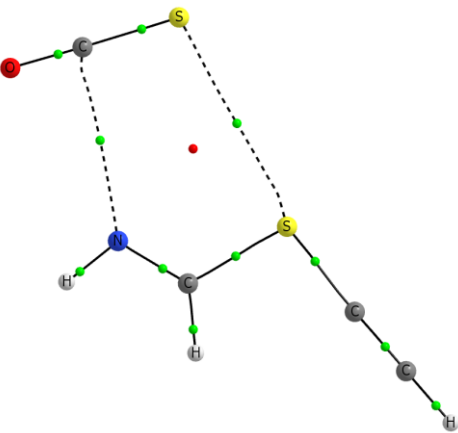
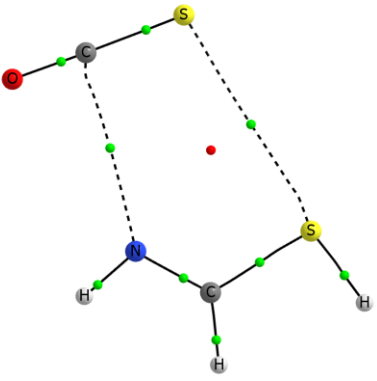
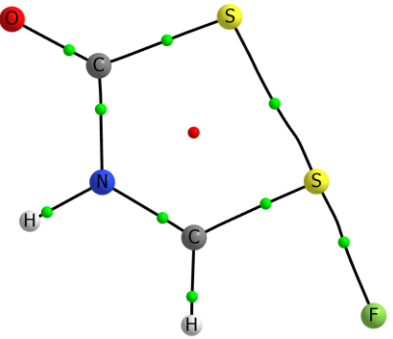
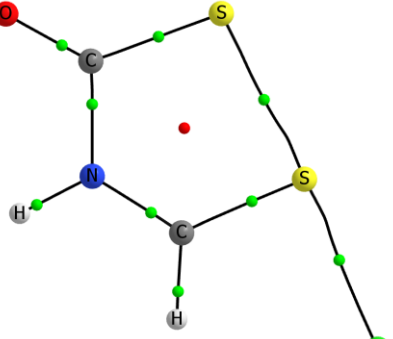
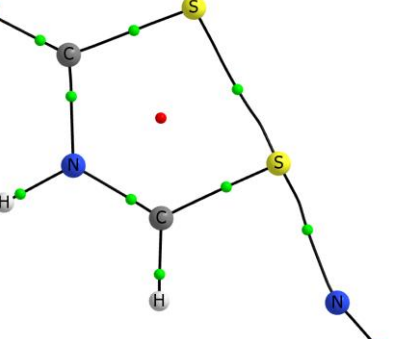
	<p>hnhscn_sco_complex  MP2= -1095.15209109 NIM= 1  C,2.8363338618,0.0520420714,0.  O,3.3394141043,1.1054432049,0.  S,2.185568671,-1.3745237355,0.  N,0.2199812178,1.667546745,0.  C,-0.9930093614,1.2989600964,0.  S,-1.3237014804,-0.454225243,0.  C,-3.0148706138,-0.3446491173,0.  H,-1.8872889443,1.9228005532,0.  H,0.2810039429,2.6858049148,0.  N,-4.1901482829,-0.2888795217,0.</p>
	<p>hnhscch_sco_complex  MP2= -1079.05817922 NIM= 1  C,2.8499161047,0.0588550591,0.  O,3.3553554619,1.1115709409,0.  S,2.1987189963,-1.3668386547,0.  N,0.2359967458,1.6635413005,0.  C,-0.9804692784,1.2939493801,0.  S,-1.3457418092,-0.4419173124,0.  C,-3.0329496815,-0.3409959917,0.  H,-1.8681096586,1.9286793753,0.  H,0.2922737051,2.6818479305,0.  C,-4.2517074712,-0.3183720594,0.  H,-5.3144243049,-0.2994035581,0.</p>
	<p>hnhsh_sco_complex  MP2= -1003.07630771 NIM= 1  C,1.7320890987,-0.646017749,0.  O,2.3572953422,0.340510009,0.  S,0.9205334934,-1.9865131691,0.  N,-0.6716846835,1.2532005561,0.  C,-1.9322723803,1.0584698426,0.  S,-2.5549533518,-0.5865501108,0.  H,-3.8425676262,-0.2250146688,0.  H,-2.6926039885,1.8398614301,0.  H,-0.4762286941,2.2538528698,0.</p>

Table S3. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO molecules

	<p>hnchsf_sco_molecule  MP2= -1102.20092699 NIM= 0  C,0.1063964564,1.350975688,0.  O,0.231183774,2.5570439469,0.  S,-1.3001833888,0.3511348492,0.  N,1.273162898,0.5132232652,0.  C,1.2034918558,-0.8048855171,0.  S,-0.2173990149,-1.6692778057,0.  F,0.7599321918,-3.1780207589,0.  H,2.1165081114,-1.3843848435,0.  H,2.1723601163,0.984028176,0.</p>
	<p>hnchsl_sco_molecule  MP2= -1462.1917678 NIM= 0  C,0.1161868026,1.4166332426,0.  O,0.2716247517,2.6174942145,0.  S,-1.3259788568,0.4641802164,0.  N,1.2615645574,0.5475908076,0.  C,1.1688783233,-0.7678480425,0.  S,-0.2783576407,-1.5987588241,0.  Cl,0.8865985927,-3.5942712801,0.  H,2.072658111,-1.3624128292,0.  H,2.1722783589,0.9972294949,0.</p>
	<p>hnchsnc_sco_molecule  MP2= -1095.0922502 NIM= 0  C,0.0787267131,1.3895684502,0.  O,0.1817233793,2.5945067875,0.  S,-1.310846511,0.3648462023,0.  N,1.2684353517,0.5725842376,0.  C,1.2381702521,-0.7414880446,0.  S,-0.1791902297,-1.6307590838,0.  N,0.9488179833,-3.2300599251,0.  H,2.1675940612,-1.2945402088,0.  H,2.1571375029,1.0651968332,0.  C,1.2948844973,-4.3700182485,0.</p>

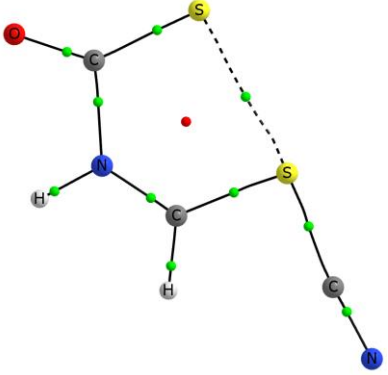
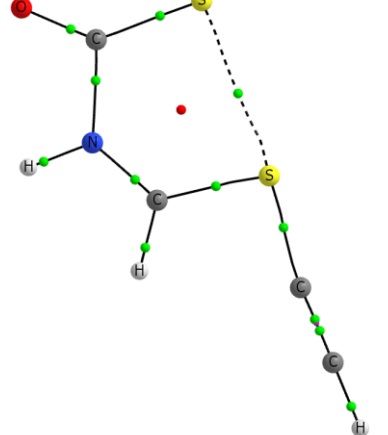
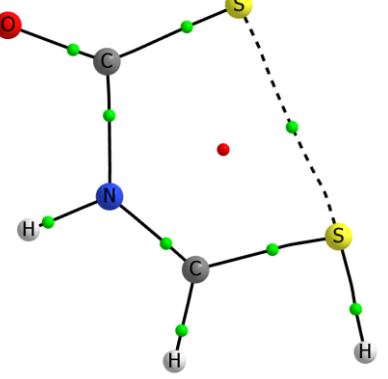
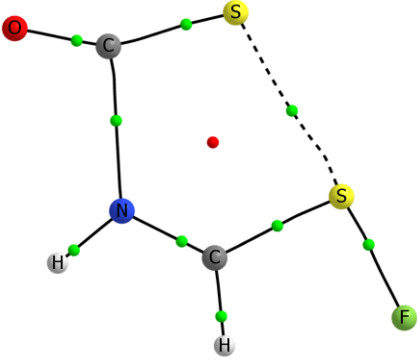
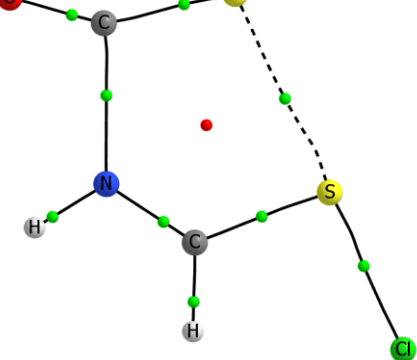
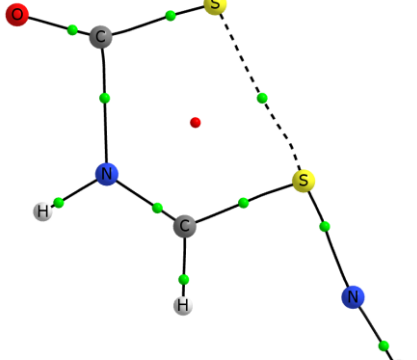
	<p>hnhscn_sco_molecule  MP2= -1095.1204361 NIM= 0  C,0.009571444,1.4320832404,0.  O,0.3186794481,2.6047735328,0.  S,-1.4221442279,0.5529594587,0.  N,1.220090029,0.5082739778,0.  C,1.2407023746,-0.7857947808,0.  S,-0.1442472918,-1.7938030826,0.  C,0.8717807877,-3.2461208971,0.  H,2.2063599189,-1.2772290275,0.  H,2.1099169207,1.004490613,0.  N,1.4347435968,-4.2797960346,0.</p>
	<p>hnhscch_sco_molecule  MP2= -1079.02817534 NIM= 0  C,-0.012510738,1.4593382669,0.  O,0.3317865051,2.625147803,0.  S,-1.454385114,0.6115119459,0.  N,1.2028977269,0.5196595892,0.  C,1.2475925176,-0.7746995867,0.  S,-0.0920458612,-1.83817435,0.  C,0.889233472,-3.2642518021,0.  H,2.2237948352,-1.245901089,0.  H,2.0872569947,1.0248105726,0.  C,1.4394293875,-4.3525142537,0.  H,1.9324032742,-5.2950900959,0.</p>
	<p>hnhsh_sco_molecule  MP2= -1003.04696789 NIM= 0  C,-1.35774839,0.17159005,0.  O,-2.45793305,0.68937447,0.  S,-0.73573469,-1.37730904,0.  N,-0.25179916,1.25422975,0.  C,1.03884101,1.14390843,0.  S,1.94147986,-0.30217892,0.  H,3.08959592,0.42288161,0.  H,1.60315247,2.06829798,0.  H,-0.64516836,2.19303285,0.</p>

Table S4. Structures (Å), total energies (a.u.) and molecular graphs of HN(CH)SX:SCO transition structures

	<p>hnchsf_sco TS  MP2= -1102.17544713 NIM= 1  C,0.0608423,-1.94405723,0.  O,0.66399223,-2.9498708,0.  S,-1.29320703,-1.05383991,0.  N,1.4626025,-0.46807969,0.  C,1.13380193,0.76849725,0.  S,-0.46972481,1.42721692,0.  F,0.12879968,3.00045113,0.  H,1.86078351,1.58010479,0.  H,2.46890802,-0.6293129,0.</p>
	<p>hnchscf_sco TS  MP2= -1462.16840470 NIM= 1  C,0.12700093,-2.31974361,0.  O,0.76871742,-3.30552958,0.  S,-1.29818323,-1.53716223,0.  N,1.41858786,-0.83596943,0.  C,1.09844807,0.40374586,0.  S,-0.53089991,1.02677632,0.  Cl,0.0922804,3.04548007,0.  H,1.84145033,1.19805858,0.  H,2.42256478,-1.01303605,0.</p>
	<p>hnchsnf_sco TS  MP2= -1095.07701872 NIM= 1  C,0.1730483003,-2.139196054,0.  O,0.8135815925,-3.1311381818,0.  S,-1.2973618812,-1.4251132347,0.  N,1.3824372683,-0.7047555131,0.  C,1.0760088642,0.5356072929,0.  S,-0.5508564413,1.1694720215,0.  N,0.0251400337,2.7913531271,0.  H,1.8296451234,1.3189296148,0.  H,2.3799644125,-0.9148899031,0.  C,0.2509527276,3.9584263503,0.</p>



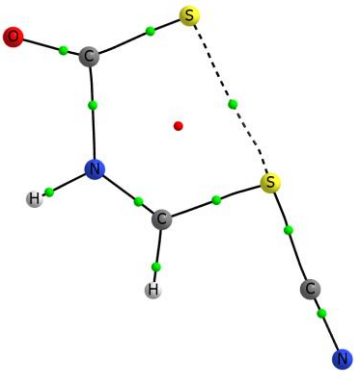
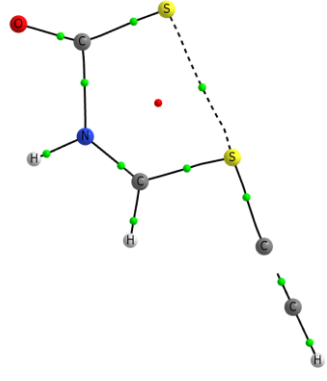
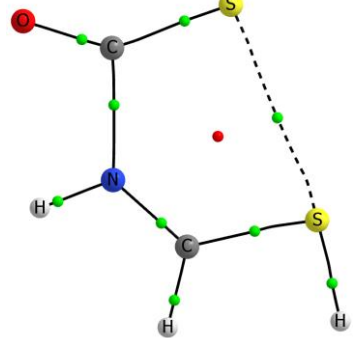
	<p>hnhscn_sco TS  MP2= -1095.11902037 NIM= 1  C,0.2462561989,-2.0721796613,0.  O,0.921117524,-3.0585386876,0.  S,-1.3119178862,-1.5367062575,0.  N,1.2994690249,-0.7129358278,0.  C,1.0291081911,0.5392586882,0.  S,-0.5808995851,1.2053291466,0.  C,0.0173114313,2.8324688387,0.  H,1.8315420202,1.2703846537,0.  H,2.2858949426,-0.9708087972,0.  N,0.3446781382,3.9624234244,0.</p>
	<p>hnhscch_sco TS  MP2= -1079.02704899 NIM= 1  C,0.2636861431,-2.1200605692,0.  O,0.9743241644,-3.0839767314,0.  S,-1.3098836561,-1.6410426669,0.  N,1.2862433521,-0.7345798379,0.  C,1.011635139,0.5199196695,0.  S,-0.5809514086,1.20527495,0.  C,-0.0335379315,2.8287437433,0.  H,1.8150905986,1.25074617,0.  H,2.2739554527,-0.9853240094,0.  C,0.2379814717,4.0170156219,0.  H,0.4833905144,5.05189587,0.</p>
	<p>hnhsh_sco TS  MP2= -1003.04605350 NIM= 1  C,0.16321793,-1.43822369,0.  O,0.80530004,-2.45067152,0.  S,-1.37485005,-0.85768913,0.  N,1.29186504,-0.13777209,0.  C,1.13951492,1.13957109,0.  S,-0.36602918,1.97742089,0.  H,0.27636136,3.16306297,0.  H,2.02574837,1.76530447,0.  H,2.25010531,-0.4823831,0.</p>

Table S5. PSO, DSO, FC, and SD components of  $^{1t}\text{J}(\text{N-C})$  and  $^{1c}\text{J}(\text{S-S})$  (Hz) for complexes, bound molecules, and transition structures with  $\text{C}_s$  symmetry

Complexes					
X =	PSO	DSO	FC	SD	$^{1t}\text{J}(\text{N-C})$
F	0.0	0.0	-0.3	0.0	-0.3
Cl	0.0	0.0	-0.3	0.0	-0.3
NC	0.0	0.0	-0.3	0.0	-0.3
CCH	0.0	0.0	-0.3	0.0	-0.3
H	0.0	0.0	-0.3	0.0	-0.3
CN	0.0	0.0	-0.3	0.0	-0.3
					$^{1c}\text{J}(\text{S-S})$
F	0.1	0.0	5.7	0.0	5.7
Cl	0.0	0.0	3.8	0.0	3.8
NC	0.0	0.0	3.6	0.0	3.6
CCH	0.0	0.0	2.1	0.0	2.1
H	0.0	0.0	1.5	0.0	1.4
CN	0.0	0.0	2.3	0.0	2.3
Molecules					
	PSO	DSO	FC	SD	$^1\text{J}(\text{N-C})$
X = F	1.7	-0.2	-9.0	-0.3	-7.8
Cl	1.6	-0.2	-8.8	-0.3	-7.6
TS					$^{1t}\text{J}(\text{N-C})$
X = F	0.2	-0.1	17.9	-0.1	17.9
Cl	0.2	-0.1	21.1	-0.2	21.0
Molecules					
	PSO	DSO	FC	SD	$^{1c}\text{J}(\text{S-S})$
X = F	-1.3	0.0	13.5	0.9	13.1
Cl	-0.5	0.0	11.7	1.5	12.7
TS					
F	0.0	0.0	22.6	0.1	22.7
Cl	0.0	0.0	21.5	0.0	21.5