Supporting Information

Weak Interactions in Interstellar Chemistry: How do Open Shell Molecules Interact with Closed Shell Molecules?

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S1. Detailed Explanation for the Choice of Level of Theory

Open shell molecules require a more careful computational handling than closed shell molecules due to the possibility of several low lying excited states.[S1] It is thus very important to validate the choice of our methodology. To compute the geometries, we intentionally avoid both the unrestricted versions of the Hartree-Fock (HF) and Moller-Plessett second order perturbation (MP2) as the methods of our choice, given the large spin contamination issues with both.[S1] We also do not use the restricted open (RO) shell formalisms due to the instability of the RO wavefunctions[S1,S2] as a result of multiple possible low lying electronic states. Density functional theory on the other hand despite being *ad hoc*, is in general known to considerably reduce spin-contamination (in a mostly empirical way).[S3] It also partly takes care of dynamic electron correlation, whose rigorous treatment involves computationally expensive multi-reference methods.[S4]

The key to working with density functional theory has always been a thorough and careful calibration.[S5] From among the various density functionals, we use the UM06-2x[S6] density functional (after calibrating with some other popular density functionals –*vide infra*) for the geometries and the zero-point energies due to the following reasons: (a) It is known to accurately describe the geometry of radicals,[S7] and (b) its superior performance in describing a plethora of different types of weak interactions.[S8] In conjunction with the UM06-2x functional we choose the aug-cc-pVTZ basis-set as a compromise between computational cost and accuracy. While there are definitely much larger basis-sets than this (and we use some of them to calibrate our results – *vide infra*), it is known to be of comparable accuracy with larger basis-sets for weak interactions,[S9] is widely used,[S10] and is hence considered optimal for this study. The geometries

reported in this paper, are all confirmed to be minimum energy structures by computing harmonic frequencies, and noting the absence of any imaginary frequency.

The geometries and energies of the ground electronic states (all doublets) of the open shell molecules used in this study (OH - $^2\Pi$, SH - $^2\Pi$, CN - $^2\Sigma^+$, NO - $^2\Pi$, NH_2 – $^2B_1$, HO_2 – ^2A") have been compared with those reported in the Computational Chemistry Comparison and Benchmark DataBase (CCCBDB) and found to be very similar to them.[S11] Also, the $<S^2>$ values for all the molecules using the UM062X/aug-cc-pVTZ geometries are found to be less than about 0.770, indicating insignificant spin-contamination. To more accurately get the energies, we use the UCCSD(T)(FC)/aug-cc-pVTZ level of theory, based on the UM06-2x/aug-cc-pVTZ geometries.[S12] It was chosen since the "gold-standard" CCSD(T) method is known to perform exceedingly well to describe weak interactions.[S13] Besides, even though the UCCSD(T) method uses a UHF wavefunction, it does not result in spin-contamination.[S14,S15] In fact, it eliminates contamination from the S+1 component, and vastly reduces the deleterious effects from the S+2 component. The S+3 and higher contributions are noticed to be negligible, thereby indicating that CCSD(T) is suitable for the present study. The energies obtained at this level of theory, are then corrected for the basis-set superposition error (BSSE) arising due to the finiteness of the basis-set used, by performing counterpoise corrections at the UCCSD(T)(FC)/aug-cc-pVTZ level of theory.[S16] Despite working with open shell systems, since we are not dealing with transition-metals/post-transition metals - for which relativistic effects and spin-orbit coupling are important, we do not make any correction for spin-orbit coupling. All the calculations are performed using the *Gaussian 09* suite of programs.[S17]

To validate our methodology for getting the geometries, we have performed additional geometry optimizations and single-point energy calculations on representative systems at various levels of

theories - UCCSD(T)(FC)/aug-cc-pVTZ//UB3-LYP(D3-BJ)/aug-cc-pVTZ, UCCSD(T)(FC)/aug-cc-pVTZ//UB2PLYP(D3-BJ)/aug-cc-pVTZ, and UCCSD(T)(FC)/aug-cc-pVTZ//UωB97X-D/aug-cc-pVTZ.[S18-S22] We also find that the inclusion of empirical dispersion corrections, to the density functionals does not change the results in the paper. Similarly, to be certain that the triple-ζ quality basis-set used is appropriate, we calculate energies at the UCCSD(T) (FC)/aug-cc-pVQZ level of theory using much larger quadruple-ζ basis-set (starting with UM062X/aug-cc-pVTZ geometries). Finally, we employ two different two-point complete-basis set (CBS) extrapolation schemes – one wherein we extrapolate only the correlation energy, and another wherein we extrapolate both the Hartree-Fock energy and the correlation energy; to get the UCCSD(T)(FC) energies at the infinite basis-set limit.[S23,S24] Overall, we find the geometries and energies to majorly be in close agreement with the UCCSD(T)(FC)/aug-cc-pVTZ//UM06-2x/aug-cc-pVTZ computations (interaction energies within ~ 1-2 kcal/mol mostly). More details of our careful calibration are provided in the supporting information.

The interaction energy (E_{int}) computed in this work is defined as follows:

Consider any gas phase open shell molecule "X" and gas phase closed shell molecule "Y" forming a weakly bound complex "XY" in the ISM, *i.e*, X (g) + Y (g) → XY(g),

$$E_{int} = E(XY) – E(X) – E(Y).$$

Where E(XY) is the zero point corrected energy of the complex, E(X) that for the open shell molecule, and E(Y) that for the closed shell molecule. The energies come from the CCSD(T) single point calculations, and the zero point corrections from M06-2x geometries (aug-cc-pVTZ basis-set used throughout).

In quantum chemistry, there is no single definitive way to ascertain the nature of the weak interactions. All the existing methods involve either some variation of using properties of electron densities, or perturbation theory/partitioning the wavefunction, and come with their own set of pros and cons. Here, we adopt three different strategies, and look for corroborations/contradictions amongst them.

Bader's atoms-in-molecules (AIM) method, based on the properties and topology of the electron densities, is used to confirm that there are weak interactions.[S25] Bond critical points are computed, and the electron densities ($\rho(r_c)$ $\nabla^2\rho(r_c)$) and the value of the Laplacian at the bond critical points ($\nabla^2\rho(r_c)$) is calculated.[S26] Having thus ascertained that weak interactions are involved here (using the well-established criteria that $\rho(r_c) \sim$ being 10^{-2} to 10^{-3} a.u, and ($\nabla 2\rho$(rc) being positive, and in the approximately 10^{-1} to 10^{-2} range),[S26] the spin densities (Mulliken spin densities)[S27] on the atoms are calculated for all the molecules, before and after they are bound together. A change in the spin densities reflect upon the fact that the interactions are not just electrostatically dominant, but also involve some orbital overlap. The local nature of orbital overlap (involving only the donor atom and the acceptor atom) is then further assessed using the natural bond orbital (NBO) method, *via* the donor-acceptor interaction energies (E2 energies) obtained from perturbation theory.[S28]

An important point to bear in mind here is that the extent of orbital overlap in these molecules is best ascertained by changes in the spin-density, as opposed to NBO calculations. This is because, the NBO method localizes the canonical Kohn Sham orbitals, and so we end up focusing solely on only the donor and acceptor atoms. Whereas, the change in spin density takes the entire molecule into account. The NBO interaction energies nonetheless provide valuable chemical insight regarding the local nature of the weak interactions.

S2. Organization of the Results and Discussion Section in the Main Text

For each of the six open shell species (OH, SH, CN, NO, NH_2, HO_2)) interacting with the closed shell molecules (H_2O, H_2S, HF, HCl, NH_3, PH_3, HCN, HNC, HCP, CH_3OH, and CH_3SH) a lot of data is generated. This is because, multiple scenarios arise, such as: (a) the closed shell molecule acting as a hydrogen bond donor and the open shell molecule acting as a hydrogen bond acceptor, (b) the opposite case, wherein the closed shell molecule acts as a hydrogen bond acceptor and the open shell molecule acting as a hydrogen bond donor (with OH, SH, NH_2 and HO_2), (c) the prevalence of other types of weak interactions (eg. Halogen bond, chalcogen bond, weak interaction involving an open shell atom etc) and (d) the co-operative functioning of multiple weak interactions in the same structure.

To make it easier on the reader, we herein explain the organization of this section. For those radicals containing a H atom themselves (OH, SH, NH_2, and HO_2), we have devoted one figure wherein we present the geometries/interaction energies when these radicals are the hydrogen bond donors. This is followed by another figure for the geometries/interaction energies where the open shell molecules are hydrogen bond acceptors. Lastly in one more figure, the other kinds of (non-hydrogen bonding) interactions (if suitable minima are found) are discussed. For the other radicals not containing the hydrogen atom (CN and NO), the possible weak interactions occurring via both the terminals of the atoms (CN and NO) are presented. Throughout, it should be noted that, in many cases multiple weak interactions are simultaneously at work, and it is difficult to uniquely assign a structure to any particular figure. Such structures are discussed in the figures deemed to be the most appropriate for them. Corresponding to each figure, one table then summarizes our NBO and AIM analysis for the structures shown in that particular figure.

Along with the tables featuring NBO and AIM analyses, the detailed spin-density information is also provided in the supporting information.

It is also useful to clarify some terminologies before glancing into the results. Conventionally, the term halogen bonding refers to the case where an electron rich atom (donor) interacts with a relatively less electron rich halogen atom (see reference 26 in the main text). Likewise, when the less electron rich atoms happen to be chalcogens or pnicogens or carbon atoms, the prevailing weak interactions are termed as chalogen bonding or pnicogen bonding or carbon bonding, respectively.[26] In all of these cases (halogen/chalcogen/pnicogen/carbon bonding) both the interacting atoms (the donor and the acceptor) have an even number of non-bonding electrons. However, in this study, since we deal with open shell species, one of them (donor or acceptor atoms) possesses an odd number of non-bonding electrons. Regardless of this aspect, we shall continue to use the same nomenclature (*viz*. halogen bonding, chalcogen bonding, pnicogen bonding, carbon bonding etc) to appropriately describe the prevailing weak interactions.

It should be noted that the phrase "orbital interaction energy" used in the SI is different from the computed "interaction energy". The "orbital interaction energy" comes from the NBO calculations and the "interaction energy" is computed as shown in the previous section (*vide supra*) and in the main text.

Structures with Positive Interaction Energies

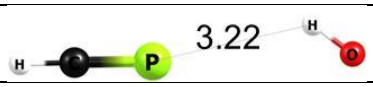
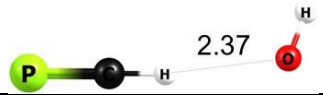
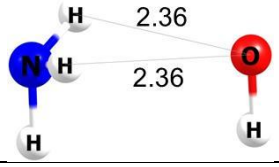
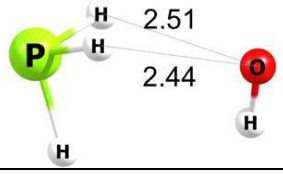
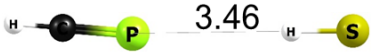
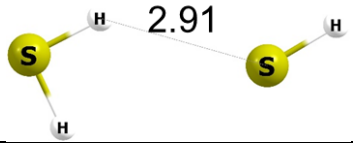
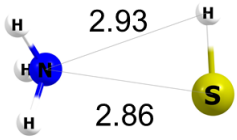
From out of a total ~ 160 minimum energy structures we obtained as part of this work, ~ 43 of them have a positive interaction energy, despite being fully optimized minimum energy structures. Such structures which result in positive interaction energies are tabulated in Table S3, and not in the main-text following the suggestions of an anonymous referee. A positive interaction energy implies that the formation of the complexes are not thermodynamically favorable.

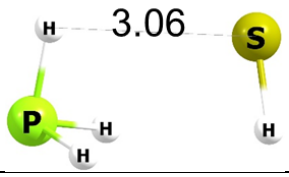
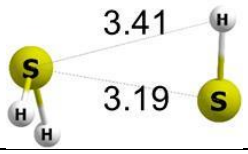
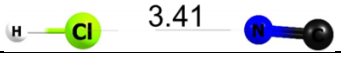
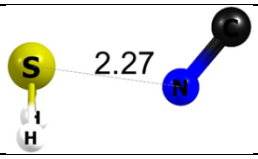
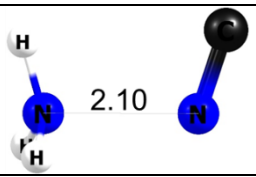
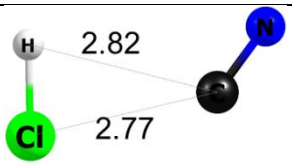
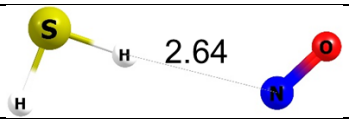
In case there are systematic errors in the computed interaction energies, they could arise due to: (a) the UCCSD(T)(FC)/aug-cc-pVTZ method's accuracy (~ 1kcal/mol), (b) the accuracy in zero point vibrational energy computation with the UM06-2x/aug-cc-pVTZ, method, or (c) during the optimization of our structures, we could have missed out on more stable isomers/lower lying electronic states. Each of these points is independently verified in the work, and we believe that we report the right isomer/electronic state, and the correct value of the interaction energies.

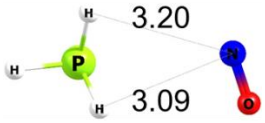
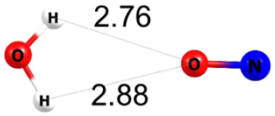
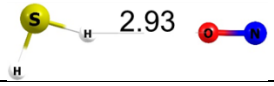
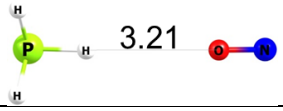
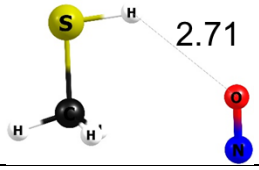
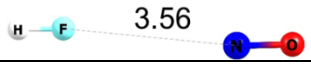
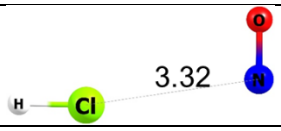
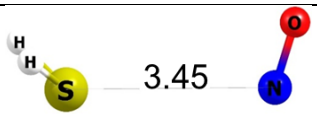
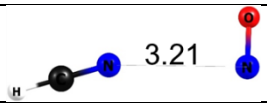
It might however definitely be possible that more accurate measures of the interaction energies can be computed/other more stable isomers or electronic states may be obtained by using much more computationally expensive methods (the kind of which we could not perform with our computational resources).

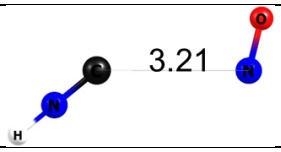
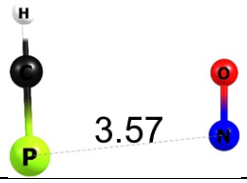
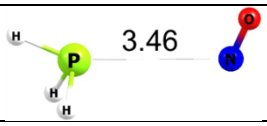
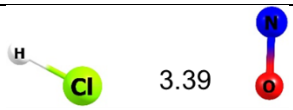
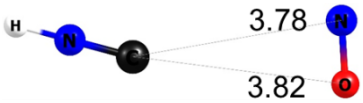
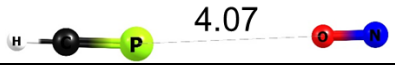
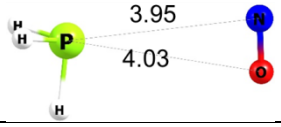
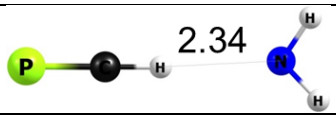
All the structures reported in Table SI_1 have doublet electronic states, and are neutral. Level of theory used – UCCSD(T)(FC)/aug-cc-pVTZ//UM06-2x/aug-cc-pvTZ. They are all minimum energy structures with zero imaginary frequencies. Computed interaction energies include ZPE and BSSE corrections.

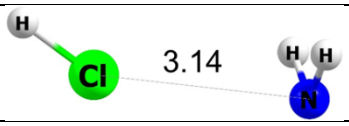
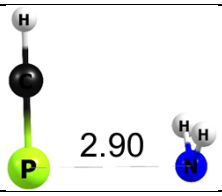
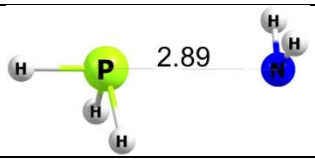
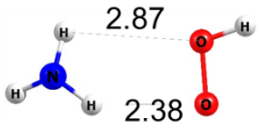
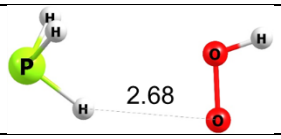
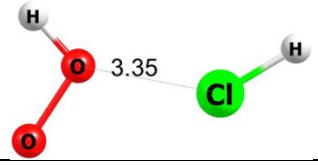
Table SI_1: Structures whose interaction energies are positive

System	Structures	Interaction energy (kcal/mol): UCCSD(T)/ aug-cc-pVTZ//UM06-2x/aug-cc-pVTZ
OH···Molecules		
$H_{OH}\cdots P_{HCP}$		1.05
	Figure S1	
$O_{OH}\cdots H_{HCP}$		0.30
	Figure S2	
$O_{OH}\cdots H_{NH3}$		0.61
	Figure S3	
$O_{OH}\cdots H_{PH3}$		0.87
	Figure S4	
SH···Molecules		
$H_{SH}\cdots Cl_{HCl}$		1.42
	Figure S5	
$H_{SH}\cdots P_{HCP}$		0.35
	Figure S6	
$S_{SH}\cdots H_{H2S}$		0.48
	Figure S7	
$S_{SH}\cdots N_{NH3}$		0.20
	Figure S8	

$S_{SH}\cdots H_{PH3}$		1.63
	Figure S9	
$S_{SH}\cdots S_{H2S}$		0.62
	Figure S10	
CN···Molecules		
$N_{CN}\cdots H_{HCP}$		0.13
	Figure S11	
$N_{CN}\cdots Cl_{HCl}$		0.85
	Figure S12	
$N_{CN}\cdots S_{H2S}$		2.86
	Figure S13	
$N_{CN}\cdots N_{NH3}$		3.74
	Figure S14	
$C_{CN}\cdots F_{HF}$		0.16
	Figure S15	
$C_{CN}\cdots Cl_{HCl}$		0.14
	Figure S16	
NO···Molecules		
$N_{NO}\cdots H_{H2S}$		0.57
	Figure S17	

$N_{NO}\cdots H_{PH3}$		0.08
	Figure S18	
$O_{NO}\cdots H_{H2O}$		0.00
	Figure S19	
$O_{NO}\cdots H_{H2S}$		0.61
	Figure S20	
$O_{NO}\cdots H_{NH3}$		0.24
	Figure S21	
$O_{NO}\cdots H_{PH3}$		0.31
	Figure S22	
$O_{NO}\cdots H_{CH3SH}$		0.19
	Figure S23	
$N_{NO}\cdots F_{HF}$		0.21
	Figure S24	
$N_{NO}\cdots Cl_{HCl}$		0.60
	Figure S25	
$N_{NO}\cdots S_{H2S}$		0.48
	Figure S26	
$N_{NO}\cdots N_{HCN}$		0.30
	Figure S27	

$N_{NO}\cdots C_{HNC}$		0.65
	Figure S28	
$N_{NO}\cdots P_{HCP}$		0.02
	Figure S29	
$N_{NO}\cdots P_{PH3}$		0.55
	Figure S30	
$O_{NO}\cdots F_{HF}$		0.50
	Figure S31	
$O_{NO}\cdots Cl_{HCl}$		0.51
	Figure S32	
$O_{NO}\cdots C_{HNC}$		0.07
	Figure S33	
$O_{NO}\cdots P_{HCP}$		0.10
	Figure S34	
$O_{NO}\cdots P_{PH3}$		0.53
	Figure S35	
$NH_2\cdots$Molecules		
$H_{NH2}\cdots Cl_{HCl}$		0.62
	Figure S36	
$N_{NH2}\cdots H_{HCP}$		0.57
	Figure S37	

$N_{NH_2}\cdots Cl_{HCl}$		0.43
	Figure S38	
$N_{NH_2}\cdots P_{HCP}$		0.37
	Figure S39	
$N_{NH_2}\cdots P_{PH_3}$		0.28
	Figure S40	
$HO_2\cdots$Molecules		
$O_{HO_2}\cdots H_{NH_3}$		0.40
	Figure S41	
$O_{HO_2}\cdots H_{PH_3}$		0.70
	Figure S42	
$O_{HO_2}\cdots Cl_{HCl}$		0.89
	Figure S43	

S3. AIM, NBO, and Spin Density Analyses for the Structures in all the Figures

AIM, NBO, and Spin Density Analyses for the Structures in Figure 1 (and Figure S1)

AIM analysis of all the species in **Figure 1** is reported in Table SI_2 (columns 4 and 5). The $\rho(r_c)$ and $\nabla^2\rho(r_c)$ confirm that weak interactions are present here.

Then, the spin densities on all the heavy atoms were computed before and after binding (after ensuring that there is no spin contamination, see Table SI_3). With the exception of Figure 1k, (binding with CH_3SH), the spin density on O (of OH radical) did not change at all after interacting with the closed shell molecules. In the case of CH_3SH however, the spin density on O (1.000 prior to binding, Table SI_3) substantially changed (~ 0.600 after binding) as some spin density was transferred to the S of CH_3SH (~0. 400) indicating some orbital overlap.

NBO calculations (Table SI_2) revealed a substantive amount of localized orbital interaction (n-σ*) in a lot of the cases (Figs. 1c-1h, 1j). The participating lone-pair orbitals (n) varies from molecule to molecule but the anti-bonding orbital (σ*) of the OH radical is always sp^3 hybridized. **Figure 1k** presents an interesting case where there is definitive spin transfer (*vide supra*). However, the NBO analysis does not show any type of local orbital interaction, either between S (of CH_3SH) and H (of OH) or S (of CH_3SH) and O (of OH).

Table SI_2: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 1 (main text) and Figure S1 (SI)**. The same level of theory used to optimize the structures in **Figure 1 (main text)** are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[d] (AIM)**	**Figure**
Insignificant	$F_{HF}\cdots H_{OH}$	-	0.0053	0.0259	1a
Insignificant	$H_{HCl}\cdots H_{OH}$	-	0.0137	0.0591	1b
− 4.12	$O_{H_2O}\cdots H_{OH}$	n (sp^2) - σ* (sp^3)	0.0266	0.0945	1c
− 2.83	$S_{H_2S}\cdots H_{OH}$	n (p) - σ* (sp^3)	0.0159	0.0392	1d
− 2.52	$N_{HCN}\cdots H_{OH}$	n (sp) - σ* (sp^3)	0.0204	0.0700	1e

− 4.18	$C_{HNC}\cdots H_{OH}$	n (sp) - σ* (sp^3)	0.0202	0.0528	1f
− 8.33	$N_{NH_3}\cdots H_{OH}$	n (sp^3) - σ* (sp^3)	0.0336	0.0729	1g
− 2.13	$P_{PH_3}\cdots H_{OH}$	n (sp) - σ* (sp^3)	0.0145	0.0323	1h
Insignificant	$P_{HCP}\cdots H_{OH}$	-	0.0036	0.0107	S1
Insignificant	$P_{HCP}\cdots H_{OH}$	-	0.0133	0.0360	1i
− 3.96	$O_{CH_3OH}\cdots H_{OH}$	n (sp) - σ* (sp^3)	0.0294	0.1036	1j
Insignificant	$S_{CH_3SH}\cdots H_{OH}$	-	0.0645	0.1334	1k

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_3: Spin density for the structures in Figure 1 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
O_{OH}	1.000	0.753	
OH_HF			
F_{HF}	-0.000	0.753	1a
O_{OH}	1.000		
OH_HCl			
Cl_{HCl}	0.009	0.753	1b
O_{OH}	0.990		
OH_NH_3			
N_{NH_3}	0.005	0.754	1c
O_{OH}	0.994		
OH_H_2O			
O_{H_2O}	0.001	0.753	1d
O_{OH}	0.998		
OH_H_2S			
S_{H_2S}	0.001	0.753	1e
O_{OH}	0.998		
OH_PH_3			
P_{PH_3}	-0.000	0.754	1f
O_{OH}	1.000		
OH_HCN			
N_{HCN}	0.003	0.753	1g

C_{HCN}	-0.000		
O_{OH}	0.996		
OH_HNC			
N_{HNC}	0.001	0.753	1h
C_{HNC}	0.003		
O_{OH}	0.994		
OH_HCP			
P_{HCP}	0.003	0.753	S1
C_{HCP}	-0.001		
O_{OH}	0.998		
OH_HCP			
P_{HCP}	-0.001	0.753	1i
C_{HCP}	0.003		
O_{OH}	0.998		
OH_CH_3OH			
C_{CH_3OH}	0.000	0.753	1j
O_{CH_3OH}	0.007		
O_{OH}	0.992		
OH_CH_3SH			
C_{CH_3SH}	0.003	0.758	1k
S_{CH_3SH}	0.411		
O_{OH}	0.584		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 2 (and Figure S2-S4)

Table SI_4 contains the AIM and NBO analysis for all the structures in **Figure 2**. The supporting information (Table SI_3) has the spin density information. As expected, the $\rho(r_c)$ and $\nabla^2\rho(r_c)$ values (Table SI_4) fall well within the range, indicating the presence of weak interactions. There is no change in the spin densities of the atoms before and after binding (Table SI_5). The NBO analysis points out to some local orbital overlap in all the cases but for those with ammonia and phosphine (**Figures S3** and **S4)**.

Given that in **Figure 2b**, the OH radical is the hydrogen bond donor, the filled n orbital of the OH radical is involved in hydrogen bonding, as opposed to its filled σ* orbital. In some cases this vacant n orbital has a pure *s* type character (with HF in **2a**, HCl in **2b**, and HNC in **2e**) or is *sp* hybridized (with H_2S in **2c** and HCP in **2f**), and also exhibits sp^3 hybridization with the other molecules in **Figure 2**. Further, the spin-density data (Table SI_5) implies that the interaction is dominated by electrostatics.

Table SI_4: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 2 (main text) and Figure S2-S4 (SI)**. The same level of theory used to optimize the structures in **Figure 2** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[d] (AIM)**	**Figure**
− 1.16	$O_{OH}\cdots H_{HF}$	n (sp) - σ* (s)	0.0159	0.0658	2a
− 1.39	$O_{OH}\cdots H_{HCl}$	n (sp) - σ* (s)	0.0146	0.0622	2b
− 1.26	$O_{OH}\cdots H_{H_2S}$	n (p) - σ* (sp^3)	0.0108	0.0390	2c
− 2.56	$O_{OH}\cdots H_{HCN}$	n (sp^3) - σ* (sp)	0.0140	0.0559	2d
− 5.05	$O_{OH}\cdots H_{HNC}$	n (sp^2) - σ* (s)	0.0233	0.0848	2e
− 0.94	$O_{OH}\cdots H_{HCP}$	n (sp^3) - σ* (sp)	0.0100	0.0378	S2
Insignificant	$O_{OH}\cdots H_{HCP}$	-	0.0158	0.0622	2f
Insignificant	$O_{OH}\cdots H_{NH_3}$	-	0.0170	0.0722	S3
Insignificant	$O_{OH}\cdots H_{PH_3}$	-	0.0128	0.0463	S4

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_5: Spin density for the structures in Figure 2 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
O_{OH}	1.000	0.753	
OH_HF			
F_{HF}	-0.004	0.753	2a
O_{OH}	1.004		
OH_HCl			
Cl_{HCl}	-0.004	0.753	2b
O_{OH}	1.004		
OH_H_2S			
S_{H_2S}	-0.000	0.753	2c
O_{OH}	1.000		
OH_HCN			
N_{HCN}	0.000	0.753	2d
C_{HCN}	-0.005		
O_{OH}	1.005		
OH_HNC			
N_{HNC}	-0.006	0.753	2e
C_{HNC}	0.001		
O_{OH}	1.004		
OH_HCP			
P_{HCP}	0.003	0.753	S2
C_{HCP}	-0.007		
O_{OH}	1.003		
OH_HCP			
P_{HCP}	0.127	0.756	2f
C_{HCP}	-0.096		
O_{OH}	0.969		
OH_NH_3			
N_{NH_3}	0.035	0.755	S3
O_{OH}	0.964		
OH_PH_3			
P_{PH_3}	0.021	0.754	S4
O_{OH}	0.978		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 3 (and Figure S5, S6)

The lack of orbital overlap is further supported by the absence of any spin density change on S (of SH) before and after the weak interactions (Table SI_7). Further, as noticed with OH radicals, AIM calculations indisputably indicate the existence of weak interactions (Table SI_6). The results of the NBO calculations (Table SI_6), imply that in most cases, locally there are substantial donor-acceptor interactions.

Table SI_6: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 3 (main text) and Figure S5, S6 (SI)**. The same level of theory used to optimize the structures in Figure 3 (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d]**	**$\nabla^2\rho(r_c)$[d]**	**Figure**
Insignificant	$F_{HF}\cdots H_{SH}$	-	0.0080	0.0368	3a
Insignificant	$Cl_{HCl}\cdots H_{SH}$	-	0.0010	0.0046	S5
− 1.90	$O_{H_2O}\cdots H_{SH}$	n (sp) - σ* (sp^3)	0.0149	0.0579	3b
− 1.48	$S_{H_2S}\cdots H_{SH}$	n (p) - σ* (sp^3)	0.0097	0.0251	3c
− 1.03	$N_{HCN}\cdots H_{SH}$	n (sp) - σ* (sp^3)	0.0107	0.0388	3d
− 1.68	$C_{HNC}\cdots H_{SH}$	n (sp) - σ* (sp^3)	0.0108	0.0320	3e
Insignificant	$P_{HCP}\cdots H_{SH}$	-	0.0022	0.0070	S6
Insignificant	$P_{HCP}\cdots H_{SH}$	-	0.0085	0.0242	3f
Insignificant	$P_{HCP}\cdots H_{SH}$	-	0.0115	0.0313	3g
− 4.07	$N_{NH_3}\cdots H_{SH}$	n (sp^3) - σ* (sp^3)	0.0187	0.0556	3h
− 1.07	$P_{PH_3}\cdots H_{SH}$	n (sp) - σ* (sp^3)	0.0086	0.0206	3i
− 1.67	$O_{CH_3OH}\cdots H_{SH}$	n (sp) - σ* (sp^3)	0.0172	0.0677	3j
− 1.20	$S_{CH_3SH}\cdots H_{SH}$	n (p) - σ* (sp^3)	0.0292	0.0530	3k

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar and provided in the SI. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_7: Spin density for the structures in Figure 3 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
S_{SH}	1.000	0.753	
SH_HF			
F_{HF}	0.001	0.753	3a
S_{SH}	0.999		
SH_HCl			
Cl_{HCl}	0.003	0.753	S5
S_{SH}	0.996		
SH_H_2O			
O_{H_2O}	0.003	0.753	3b
S_{SH}	0.996		
SH_H_2S			
S_{H_2S}	0.000	0.753	3c
S_{SH}	0.999		
SH_HCN			
N_{HCN}	0.005	0.753	3d
C_{HCN}	0.002		
S_{SH}	0.992		
SH_HNC			
N_{HNC}	0.003	0.753	3e
C_{HNC}	0.008		
S_{SH}	0.987		
SH_HCP			
P_{HCP}	0.001	0.753	S6
C_{HCP}	-0.002		
S_{SH}	1.000		
SH_HCP			
P_{HCP}	-0.002	0.753	3f
C_{HCP}	0.006		
S_{SH}	0.995		
SH_HCP			
P_{HCP}	0.080	0.755	3g
C_{HCP}	-0.056		
S_{SH}	0.975		
SH_NH_3			
N_{NH_3}	0.009	0.753	3h
S_{SH}	0.990		
SH_PH_3			

P_{PH_3}	0.002	0.753	3i
S_{SH}	0.997		
SH_CH_3OH			
C_{CH_3OH}	-0.0	0.753	3j
O_{CH_3OH}	0.0		
S_{SH}	0.9		
SH_CH_3SH			
C_{CH_3SH}	-0.004	0.754	3k
S_{CH_3SH}	-0.010		
S_{SH}	1.015		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 4 (and Figure S7-S9)

Interestingly, the spin density on S (of SH) before and after interacting with NH_3 did not change at all. NBO analysis (Table SI_8) also reveals that there is no interaction between the S of SH, and N of NH_3. The structure in **Figure 4h** however does lead to some change in the spin density on S (Table SI_9). After interacting with CH_3SH, some spin on S (of SH – spin density of 1 before binding and only 0.8 after binding) is transferred to S of CH_3SH (spin density of 0.8). The NBO method however does not show any donor-acceptor type interaction between the two sulfur atoms (Table SI_9).

Table SI_8: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 4 (main text) and Figure S7-S9 (SI)**. The same level of theory used to optimize the structures in **Figure 4** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d]**	**$\nabla^2\rho(r_c)$[e]**	**Figure**
− 5.95	$S_{SH}\cdots H_{HF}$	n (p) - σ* (s)	0.0225	0.0453	4a
− 4.49	$S_{SH}\cdots H_{HCl}$	n (p) - σ* (s)	0.0164	0.0381	4b
− 2.08	$S_{SH}\cdots H_{H_2O}$	n (p) - σ* (sp^3)	0.0140	0.0376	4c
− 0.60	$S_{SH}\cdots H_{H_2S}$	n (p) - σ* (sp^3)	0.0074	0.0206	S7
− 2.48	$S_{SH}\cdots H_{HCN}$	n (sp^3) - σ* (sp)	0.0102	0.0277	4d
− 4.62	$S_{SH}\cdots H_{HNC}$	n (p) - σ* (s)	0.0158	0.0394	4e
− 0.76	$S_{SH}\cdots H_{HCP}$	n (p) - σ* (sp)	0.0071	0.0196	4f
Insignificant	$S_{SH}\cdots H_{NH_3}$	-	0.0191	0.0560	S8
Insignificant	$S_{SH}\cdots H_{PH_3}$	-	0.0085	0.0250	S9
− 1.65	$S_{SH}\cdots H_{CH_3OH}$	n (p) - σ* (sp^3)	0.0127	0.0349	4g
Insignificant	$S_{SH}\cdots S_{CH_3SH}$	-	0.0336	0.0546	4h

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_9: Spin density for the structures in Figure 4 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	**Spin Density**	**$<S^2>$ Value**	**Figure**
S_{SH}	1.000	0.753	
SH_HF			
F_{HF}	0.008	0.753	4a
S_{SH}	0.991		
SH_HCl			
Cl_{HCl}	0.003	0.753	4b
S_{SH}	0.996		
SH_H_2O			
O_{H_2O}	0.006	0.753	4c
S_{SH}	0.993		
SH_H_2S			

S_{H_2S}	0.000	0.753	S7
S_{SH}	0.999		
SH_HCN			
N_{HCN}	0.000	0.753	4d
C_{HCN}	0.000		
S_{SH}	0.998		
SH_HNC			
N_{HNC}	0.010	0.753	4e
C_{HNC}	-0.002		
S_{SH}	0.992		
SH_HCP			
P_{HCP}	0.001	0.753	4f
C_{HCP}	-0.002		
S_{SH}	1.000		
SH_NH_3			
N_{NH_3}	0.046	0.754	S8
S_{SH}	0.953		
SH_PH_3			
P_{PH_3}	0.002	0.753	S9
S_{SH}	0.997		
SH_CH_3OH			
C_{CH_3OH}	-0.002	0.753	4g
O_{CH_3OH}	0.004		
S_{SH}	0.997		
SH_CH_3SH			
C_{CH_3SH}	0.003	0.755	4h
S_{CH_3SH}	0.197		
S_{SH}	0.799		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 5 (and Figure S10)

Some electron density gets transferred from S to P. Prior to binding the spin density on S is 1 (Table SI_11). After binding with PH_3 it reduces to 0.8, and the spin density on P becomes 0.2. In addition to the spin density transfer, the NBO analysis (Table SI_10) also shows a substantial donor (an n type sp^3 orbital on S)-acceptor (a σ* type s orbital on P) orbital interaction energy (Table SI_10).

Table SI_10: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 5 (main text) and Figure S10 (SI)**. The same level of theory used to optimize the structures in **Figure 5** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
Insignificant	$S_{SH}\cdots O_{H_2O}$	-	0.0145	0.0500	5a
Insignificant	$S_{SH}\cdots S_{H_2S}$	-	0.0166	0.0392	S10
− 0.68	$S_{SH}\cdots N_{HCN}$	n (p) - σ* (p)	0.0097	0.0353	5b
− 2.38	$S_{SH}\cdots C_{HNC}$	n (p) - σ* (p)	0.0161	0.0437	5c
− 8.59	$S_{SH}\cdots P_{HCP}$	n (p) - σ* (p)	0.1210	-0.1603	5d
− 17.77	$S_{SH}\cdots P_{PH_3}$	n (sp^3) - σ* (s)	0.0617	0.0284	5e
Insignificant	$S_{SH}\cdots O_{CH_3OH}$	-	0.0169	0.0581	5f

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_11: Spin density for the structures in Figure 5 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	**Spin Density**	**$<S^2>$ Value**	**Figure**
S_{SH}	1.000	0.753	
SH_H_2O			
O_{H_2O}	0.008	0.754	5a
S_{SH}	0.991		
SH_H_2S			
S_{H_2S}	0.057	0.754	S10
S_{SH}	0.942		
SH_HCN			
N_{HCN}	-0.011	0.754	5b
C_{HCN}	0.009		
S_{SH}	1.002		
SH_HNC			
N_{HNC}	0.013	0.755	5c
C_{HNC}	0.009		
S_{SH}	0.977		
SH_ HCP			

P_{HCP}	-0.140	0.780	5d
C_{HCP}	1.071		
S_{SH}	0.068		
SH_PH$_3$			
P_{PH_3}	0.473	0.756	5e
S_{SH}	0.526		
SH_CH$_3$OH			
C_{CH_3OH}	0.001	0.754	5f
O_{CH_3OH}	0.002		
S_{SH}	0.996		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 6 (and Figure S11)

There also seems to be a qualitative correlation between the orbital interaction energy as predicted by NBO calculations (Table SI_12), and the actually calculated interaction energies (**Figure 6)**, and the AIM calculations visibly establish the presence of weak interactions. A noteworthy absence from **Figure 6** is that of the structure corresponding to the interaction of CH_3SH with CN – the CCSD(T) calculation for which did not converge to the right electronic state, despite several careful attempts.

Table SI_12: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 6 (main text) and Figure S11 (SI)**. The same level of theory used to optimize the structures in **Figure 6** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Naturl Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 4.66	$N_{CN}\cdots H_{HF}$	n (sp) - σ* (sp^3)	0.0266	0.0800	6a
− 2.66	$N_{CN}\cdots H_{HCl}$	n (sp) - σ* (sp^3)	0.0165	0.0580	6b
− 1.19	$N_{CN}\cdots H_{H_2O}$	n (sp) - σ* (sp^3)	0.0149	0.0557	6c
− 0.52	$N_{CN}\cdots H_{H_2S}$	n (sp) - σ* (sp^3)	0.0082	0.0295	6d
− 2.27	$N_{CN}\cdots H_{HCN}$	n (sp) - σ* (sp)	0.0122	0.0471	6e

− 4.57	$N_{CN}\cdots H_{HNC}$	n (sp) - σ* (sp)	0.0197	0.0690	6f
− 0.84	$N_{CN}\cdots H_{HCP}$	n (sp) - σ* (sp)	0.0081	0.0306	S11
Insignificant	$N_{CN}\cdots H_{NH3}$	-	0.0080	0.0309	6g
Insignificant	$N_{CN}\cdots H_{PH3}$	-	0.0032	0.0113	6h
− 1.12	$N_{CN}\cdots H_{CH3OH}$	n (sp) - σ* (sp^3)	0.0146	0.0555	6i

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_13: Spin density for the structures in Figure 6 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
C_{CN}	1.003	0.765	
N_{CN}	-0.003		
CN_HF			
F_{HF}	0.003	0.767	6a
C_{CN}	1.027		
N_{CN}	-0.030		
CN_HCl			
Cl_{HCl}	-0.006	0.766	6b
C_{CN}	1.017		
N_{CN}	-0.011		
CN_H_2O			
O_{H2O}	-0.003	0.766	6c
C_{CN}	1.009		
N_{CN}	-0.005		
CN_H_2S			
S_{H2S}	-0.006	0.766	6d
C_{CN}	0.995		
N_{CN}	0.011		
CN_HCN			
N_{HCN}	-0.000	0.766	6e
C_{HCN}	-0.009		
C_{CN}	1.037		

N_{CN}	-0.028		
CN_HNC			
N_{HNC}	0.007	0.767	6f
C_{HNC}	-0.000		
C_{CN}	1.032		
N_{CN}	-0.039		
CN_HCP			
P_{HCP}	-0.001	0.766	S11
C_{HCP}	-0.013		
C_{CN}	-0.023		
N_{CN}	1.038		
CN_NH_3			
N_{NH_3}	-0.005	0.766	6g
C_{CN}	0.999		
N_{CN}	0.006		
CN_PH_3			
P_{PH_3}	-0.005	0.765	6h
C_{CN}	0.998		
N_{CN}	0.006		
CN_CH_3OH			
C_{CH_3OH}	0.001	0.766	6i
O_{CH_3OH}	-0.005		
C_{CN}	1.014		
N_{CN}	-0.010		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 7 (and Figure S12-S14)

AIM analysis (Table SI_14) confirms the presence of weak interactions, but the NBO calculations show no appreciable donor acceptor interaction. A very similar scenario is seen in **Figure S14**, in the interaction with NH_3 – about two-fifth of C's spin density being transferred to N (of ammonia) and one-third to N (from CN). Remarkably, in both the cases the interaction energy is unexpectedly positive (and has been verified with others levels of theories also). We say "unexpectedly" because we see favourable N···S (in **S13**) and $N_{CN}\cdots N_{NH3}$ (in **S14**) distances

and sufficient transfer of spin density to anticipate stabilizing pnicogen bonding. Yet puzzlingly, the interaction energies are positive. The much higher values of $\nabla^2\rho$ values at the bond critical points in both **S13** and **S14** (about 0.1) relative to the other structures in **Figure 7** does provide some indication that the interaction is repulsive here. However, we are unable to offer a chemically intuitive reason for this observation.

In **Figure 7b**, after interacting with CN, the spin-density on the "P" of PH_3 is ~0.8, and that on C and N about 0.1 each (Table SI_15). Coupled with this data, the very short P•••N distance, the highly favourable interaction energy and the AIM analysis (larger $\rho(r_c)$ value – Table 7) and point out to a more or less fully formed covalent bond between P and N. The NBO calculation also indicates substantial orbital overlap (Table SI_14). Even though this is not strictly speaking a "weak interaction", we have included this data to showcase the interesting chemistry possible in the ISM.

Table SI_14: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 7 (main text) and Figure S12-S14 (SI)**. The same level of theory used to optimize the structures in **Figure 7** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
Insignificant	$Cl_{HCl}\cdots N_{CN}$	-	0.0041	0.0183	S12
Insignificant	$S_{H_2S}\cdots N_{CN}$	-	0.0643	0.0995	S13
Insignificant	$P_{HCP}\cdots N_{CN}$	-	0.0022	0.0074	7a
Insignificant	$N_{CN}\cdots N_{NH_3}$	-	0.0633	0.1467	S14
− 8.65	$P_{PH_3}\cdots N_{CN}$	n (sp) - σ* (p)	0.1225	0.0301	7b
− 6.20	$S_{CH_3SH}\cdots N_{CN}$	n (p) - σ* (p)	0.0675	0.0988	7c

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_15: Spin density for the structures in Figure 7 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
C_{CN}	1.003	0.765	
N_{CN}	-0.003		
CN_HCl			
Cl_{HCl}	-0.001	0.765	S12
C_{CN}	1.009		
N_{CN}	-0.007		
CN_H_2S			
S_{H_2S}	0.495	0.757	S13
C_{CN}	0.215		
N_{CN}	0.289		
CN_HCP			
P_{HCP}	-0.004	0.765	7a
C_{HCP}	0.001		
C_{CN}	1.017		
N_{CN}	-0.014		
CN_NH_3			
N_{NH_3}	0.423	0.758	S14
C_{CN}	0.279		
N_{CN}	0.297		
CN_PH_3			
P_{PH_3}	0.792	0.754	7b
C_{CN}	0.105		
N_{CN}	0.101		
CN_CH_3SH			
C_{CH_3SH}	0.016	0.756	7c
S_{CH_3SH}	0.538		
C_{CN}	0.200		
N_{CN}	0.244		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 8 (and Figure S15, S16)

Throughout **S15, S16, 8a and 8b**, there is no spin density transfer (Table SI_17). In **8b** (with H_2S), **8d** (with H_3N), **8e** (with CH_3OH) and **8f** (with CH_3SH), the interaction energy much

higher, and this is consistently accompanied by a spin density transfer from C_{CN} to the electronegative atom in the closed shell molecule (with the sole exception in **Figure 8e** - there isn't any significant spin density transfer from C_{CN} to O of CH_3OH). The NBO analysis is also given in Figure SI_16.

Table SI_16: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 8 (main text) and Figure S15, S16 (SI)**. The same level of theory used to optimize the structures in **Figure 8** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 0.57	$F_{HF}\cdots C_{CN}$	n (p) - σ* (p)	0.0150	0.0583	S15
Insignificant	$Cl_{HCl}\cdots C_{CN}$	-	0.0232	0.0574	S16
− 3.79	$O_{H2O}\cdots C_{CN}$	n (p) - σ* (p)	0.0419	0.1156	8a
− 8.30	$S_{H2S}\cdots C_{CN}$	n (p) - σ* (p)	0.0611	0.0613	8b
− 1.08	$N_{HCN}\cdots C_{CN}$	n (sp) - σ* (sp)	0.0157	0.0539	8c
− 15.84	$N_{NH3}\cdots C_{CN}$	n (sp^3) - σ* (sp)	0.0763	0.1007	8d
− 5.23	$O_{CH3OH}\cdots C_{CN}$	n (p) - σ* (p)	0.0565	0.1352	8e
− 12.16	$S_{CH3SH}\cdots C_{CN}$	n (p) - σ* (p)	0.0659	0.0585	8f

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_17: Spin density for the structures in Figure 8 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	**Spin Density**	**$<S^2>$ Value**	
C_{CN}	1.003	0.765	
N_{CN}	-0.003		
CN_HF			
F_{HF}	0.001	0.767	S15
C_{CN}	1.039		

N_{CN}	-0.040		
CN_HCl			
Cl_{HCl}	0.061	0.767	S16
C_{CN}	0.989		
N_{CN}	-0.051		
CN_H_2O			
O_{H_2O}	0.084	0.767	8a
C_{CN}	0.996		
N_{CN}	-0.081		
CN_H_2S			
S_{H_2S}	0.343	0.757	8b
C_{CN}	0.684		
N_{CN}	-0.027		
CN_HCN			
N_{HCN}	0.039	0.768	8c
C_{HCN}	-0.012		
C_{CN}	1.049		
N_{CN}	-0.075		
CN_NH_3			
N_{NH_3}	0.042	0.756	8d
C_{CN}	0.700		
N_{CN}	0.257		
CN_CH_3OH			
C_{CH_3OH}	0.019	0.763	8e
O_{CH_3OH}	0.122		
C_{CN}	0.941		
N_{CN}	-0.083		
CN_CH_3SH			
C_{CH_3SH}	-0.004	0.756	8f
S_{CH_3SH}	0.380		
C_{CN}	0.654		
N_{CN}	-0.030		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 9 (and Figure S17, S18)

The spin density analysis (Table SI_19) is in accord with our chemical intuition that there should be no changes in the spin densities on N and O (of NO) before and after interacting – confirming that the interactions are electrostatically dominated. The NBO analysis indicates some local orbital interaction (Table SI_18). AIM analysis also attests to the presence of weak interactions.

Table SI_18: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 9 (main text) and Figure S17, S18 (SI)**. The same level of theory used to optimize the structures in **Figure 9** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 4.16	$N_{NO}\cdots H_{HF}$	n (p)−σ* (sp^3)	0.0199	0.0150	9a
− 2.73	$N_{NO}\cdots H_{HCl}$	n (p)−σ* (sp^3)	0.0128	0.0412	9b
− 1.24	$N_{NO}\cdots H_{H_2O}$	n (p)−σ* (sp^3)	0.0116	0.0411	9c
− 0.81	$N_{NO}\cdots H_{H_2S}$	n (p)−σ* (sp^3)	0.0068	0.0219	S17
− 1.51	$N_{NO}\cdots H_{HCN}$	n (p) - σ* (sp)	0.0083	0.0298	9d
− 3.06	$N_{NO}\cdots H_{HNC}$	n (sp^3) - σ* (sp)	0.0137	0.0478	9e
Insignificant	$N_{NO}\cdots H_{HCP}$	-	0.0058	0.0200	9f
Insignificant	$N_{NO}\cdots H_{PH_3}$	-	0.0068	0.0225	S18
− 0.65	$N_{NO}\cdots H_{CH_3OH}$	n (p) - σ* (sp^3)	0.0100	0.0348	9g
Insignificant	$N_{NO}\cdots H_{CH_3SH}$	n (p) - σ* (sp^3)	0.0059	0.0187	9h

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_19: Spin density for the structures in Figure 9 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	**Spin Density**	**$<S^2>$ Value**	**Figure**
N_{NO}	0.722	0.754	
O_{NO}	0.277		
NO_HF			
F_{HF}	0.013	0.753	9a
N_{NO}	0.687		
O_{NO}	0.299		
NO_HCl			
Cl_{HCl}	0.004	0.754	9b
N_{NO}	0.706		
O_{NO}	0.288		
NO_H_2O			
O_{H_2O}	0.001	0.754	9c

N_{NO}	0.712		
O_{NO}	0.286		
NO_H_2S			
S_{H2S}	-0.002	0.754	S17
N_{NO}	0.718		
O_{NO}	0.283		
NO_HCN			
N_{HCN}	-0.003	0.754	9d
C_{HCN}	0.001		
N_{NO}	0.710		
O_{NO}	0.290		
NO_HNC			
N_{HNC}	0.013	0.754	9e
C_{HNC}	-0.001		
N_{NO}	0.691		
O_{NO}	0.296		
NO_HCP			
P_{HCP}	0.001	0.754	9f
C_{HCP}	-0.006		
N_{NO}	0.719		
O_{NO}	0.284		
NO_PH_3			
P_{PH3}	-0.001	0.754	S18
N_{NO}	0.730		
O_{NO}	0.271		
NO_CH_3OH			
C_{CH3OH}	-0.007	0.754	9g
O_{CH3OH}	0.008		
N_{NO}	0.732		
O_{NO}	0.266		
NO_CH_3SH			
C_{CH3SH}	-0.003	0.754	9h
S_{CH3SH}	0.000		
N_{NO}	0.738		
O_{NO}	0.263		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 10 (and Figure S19-S23)

AIM analysis confirms the presence of weak interactions (Table SI_20). NBO (Table SI_20) calculations mostly suggest that there are no local interactions. Lastly, spin-density computations (Table SI_21) rule out any significant orbital overlap, and support the dominance of electrostatic effects.

Table SI_20: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 10 (main text) and Figure S19-S23 (SI)**. The same level of theory used to optimize the structures in **Figure 10** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 1.52	$O_{NO}\cdots H_{HF}$	n (p) - σ* (sp^3)	0.0159	0.0620	10a
− 0.84	$O_{NO}\cdots H_{HCl}$	n (p) - σ* (sp^3)	0.0093	0.0351	10b
Insignificant	$O_{H_2O}\cdots O_{NO}$	-	0.0043	0.0186	S19
Insignificant	$O_{NO}\cdots H_{H_2S}$	-	0.0022	0.0100	S20
− 0.52	$O_{NO}\cdots H_{HCN}$	n (p) - σ* (sp)	0.0066	0.0268	10c
− 1.27	$O_{NO}\cdots H_{HNC}$	n (p) - σ* (sp)	0.0110	0.0454	10d
Insignificant	$O_{NO}\cdots H_{HCP}$	-	0.0031	0.0139	10e
Insignificant	$O_{NO}\cdots H_{NH_3}$	-	0.0021	0.0098	S21
Insignificant	$O_{NO}\cdots H_{PH_3}$	-	0.0014	0.0061	S22
Insignificant	$O_{NO}\cdots H_{CH_3OH}$	-	0.0084	0.0321	10f
Insignificant	$O_{NO}\cdots H_{CH_3SH}$	-	0.0054	0.0187	S23

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_21: Spin density for the structures in Figure 10 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
N_{NO}	0.722	0.754	
O_{NO}	0.277		
NO_HF			
F_{HF}	0.003	0.754	10a
N_{NO}	0.743		
O_{NO}	0.252		
NO_HCl			
Cl_{HCl}	0.000	0.754	10b
N_{NO}	0.734		
O_{NO}	0.265		
NO_H_2O			
O_{H2O}	-0.000	0.754	S19
N_{NO}	0.745		
O_{NO}	0.255		
NO_H_2S			
S_{H2S}	-0.000	0.754	S20
N_{NO}	0.736		
O_{NO}	0.264		
NO_HCN			
N_{HCN}	-0.001	0.754	10c
C_{HCN}	0.002		
N_{NO}	0.737		
O_{NO}	0.261		
NO_HNC			
N_{HNC}	0.002	0.754	10d
C_{HNC}	0.000		
N_{NO}	0.744		
O_{NO}	0.252		
NO_HCP			
P_{HCP}	0.002	0.754	10e
C_{HCP}	-0.004		
N_{NO}	0.745		
O_{NO}	0.255		
NO_NH_3			
N_{NH3}	-0.001	0.754	S21
N_{NO}	0.737		
O_{NO}	0.263		
NO_PH_3			
P_{PH3}	-0.000	0.754	S22
N_{NO}	0.737		
O_{NO}	0.263		
NO_CH_3OH			

C_{CH_3OH}	-0.003	0.754	10f
O_{CH_3OH}	0.000		
N_{NO}	0.748		
O_{NO}	0.254		
NO_CH$_3$SH			
C_{CH_3SH}	-0.005	0.754	S23
S_{CH_3SH}	-0.000		
N_{NO}	0.745		
O_{NO}	0.260		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 11 (and Figure S24-S30)

AIM analysis confirms weak interactions. NBO and spin-density calculations throughout confirm that there is no significant orbital overlap (Tables SI_22 and SI_23)

Table SI_22: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 11 (main text) and Figure S24-S30 (SI)**. The same level of theory used to optimize the structures in **Figure 11** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
Insignificant	$H_{HF}\cdots N_{NO}$	-	0.0013	0.0063	S24
Insignificant	$Cl_{HCl}\cdots N_{NO}$	-	0.0056	0.0220	S25
–0.65	$O_{H_2O}\cdots N_{NO}$	n (sp^3) – σ* (p)	0.0097	0.0401	11a
Insignificant	$S_{H_2S}\cdots N_{NO}$	-	0.0052	0.0184	S26
Insignificant	$N_{HCN}\cdots N_{NO}$	-	0.0055	0.0211	S27
Insignificant	$C_{HNC}\cdots N_{NO}$	-	0.0068	0.0223	S28
Insignificant	$P_{HCP}\cdots N_{NO}$	-	0.0052	0.0144	S29
–0.66	$N_{NH3}\cdots N_{NO}$	n (sp^3) – σ* (p)	0.0092	0.0358	11b
Insignificant	$P_{PH_3}\cdots N_{NO}$	-	0.0058	0.0183	S30
Insignificant	$O_{CH_3OH}\cdots N_{NO}$	-	0.0100	0.0462	11c
Insignificant	$S_{CH_3SH}\cdots N_{NO}$	-	0.0078	0.0279	11d

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c.

Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_23: Spin density for the structures in Figure 11 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
N_{NO}	0.722	0.754	
O_{NO}	0.277		
NO_HF			
F_{HF}	0.000	0.754	S24
N_{NO}	0.724		
O_{NO}	0.275		
NO_HCl			
Cl_{HCl}	-0.000	0.754	S25
N_{NO}	0.728		
O_{NO}	0.271		
NO_H_2O			
O_{H2O}	0.002	0.754	11a
N_{NO}	0.711		
O_{NO}	0.286		
NO_H_2S			
S_{H2S}	0.003	0.754	S26
N_{NO}	0.715		
O_{NO}	0.281		
NO_HCN			
N_{HCN}	0.002	0.754	S27
C_{HCN}	0.001		
N_{NO}	0.713		
O_{NO}	0.282		
NO_HNC			
N_{HNC}	-0.000	0.754	S28
C_{HNC}	0.005		
N_{NO}	0.713		
O_{NO}	0.281		
NO_HCP			
P_{HCP}	-0.036	0.754	S29
C_{HCP}	0.038		
N_{NO}	0.735		

O_{NO}	0.262		
NO_NH_3			
N_{NH3}	0.001	0.754	11b
N_{NO}	0.715		
O_{NO}	0.283		
NO_PH_3			
P_{PH3}	0.003	0.754	S30
N_{NO}	0.714		
O_{NO}	0.282		
NO_CH_3OH			
C_{CH3OH}	0.002	0.754	11c
O_{CH3OH}	0.000		
N_{NO}	0.713		
O_{NO}	0.284		
NO_CH_3SH			
C_{CH3SH}	0.005	0.754	11d
S_{CH3SH}	-0.007		
N_{NO}	0.724		
O_{NO}	0.276		

AIM, NBO, and Spin Density Analyses for the Structures in Figure S31-S35

AIM analysis confirms weak interactions. NBO and spin-density calculations throughout confirm that there is no significant orbital overlap (Tables SI_24 and SI_25). Furthermore, in **S34**, even though a minimum energy structure is obtained, no hydrogen bonding critical point was evaluated using AIM (hence the lack of entry in Table 12 for $\rho(r_c)$ and $\nabla^2\rho(r_c)$ for the structure in Figure S34). This is consistent with the much larger P•••O distance (~ 4.7 Å) in **S34**.

Table SI_24: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure S31-S35 (SI)**. The same level of theory used to optimize the structures in **Figure S31-S35** are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
Insignificant	$H_{HF}\cdots N_{NO}$	-	0.0032	0.0165	S31
Insignificant	$Cl_{HCl}\cdots N_{NO}$	-	0.0043	0.0181	S32
Insignificant	$O_{HCN}\cdots N_{NO}$	-	0.0022	0.0071	S33

Insignificant	$P_{HCP}\cdots N_{NO}$	-	-	-	S34
Insignificant	$N_{PH_3}\cdots N_{NO}$	-	0.0025	0.0078	S35

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_25: Spin density for the structures in Figure **S31-S35** (**SI**). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
N_{NO}	0.722	0.754	
O_{NO}	0.277		
NO_HF			
F_{HF}	-0.001	0.754	S31
N_{NO}	0.728		
O_{NO}	0.272		
NO_HCl			
Cl_{HCl}	0.001	0.754	S32
N_{NO}	0.730		
O_{NO}	0.268		
NO_HNC			
N_{HNC}	-0.007	0.754	S33
C_{HNC}	0.008		
N_{NO}	0.727		
O_{NO}	0.271		
NO_HCP			
P_{HCP}	-0.003	0.754	S34
C_{HCP}	0.002		
N_{NO}	0.741		
O_{NO}	0.258		
NO_PH_3			
P_{PH_3}	0.002	0.754	S35
N_{NO}	0.717		
O_{NO}	0.279		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 12 (and Figure S36)

That weak interactions are present in Figure 12, is confirmed by AIM analysis (Table SI_26). NBO calculations suggest some local orbital interactions. However, spin density analysis (Table SI_27) clearly indicates that the interactions are dominated by electrostatics (no change in spin density on N of NH_2, before and after binding).

Table SI_26: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 12 (main text) and Figure S36 (SI)**. The same level of theory used to optimize the structures in **Figure 12** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
Insignificant	$Cl_{HCl}\cdots H_{NH_2}$	-	0.0067	0.0223	S36
− 0.61	$N_{HCN}\cdots H_{NH_2}$	n (sp) - σ* (sp^3)	0.0107	0.0401	12a
− 1.01	$C_{HNC}\cdots H_{NH_2}$	n (sp) - σ* (sp^3)	0.0104	0.0323	12b
− 2.33	$N_{NH_3}\cdots H_{NH_2}$	n (sp^3) - σ* (sp^3)	0.0163	0.0527	12c
− 0.60	$P_{PH_3}\cdots H_{NH_2}$	n (sp) - σ* (sp^3)	0.0079	0.0199	12d
− 1.03	$O_{CH_3OH}\cdots H_{NH_2}$	n (sp) - σ* (sp^3)	0.0217	0.0852	12e

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_27: Spin density for the structures in Figure 12 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	**Spin Density**	**$<S^2>$ Value**	**Figure**
N_{NH_2}	1.000	0.754	
NH_2_HCl			
Cl_{HCl}	0.000	0.754	S36
N_{NH_2}	0.999		
NH_2_HCN			
N_{HCN}	0.001	0.754	12a

C_{HCN}	0.003		
N_{NH_2}	0.994		
NH_2_HNC			
N_{HNC}	0.003	0.754	12b
C_{HNC}	0.006		
N_{NH_2}	0.990		
NH_2_NH_3			
N_{NH_3}	0.008	0.754	12c
N_{NH_2}	0.991		
NH_2_PH_3			
P_{PH_3}	0.001	0.754	12d
N_{NH_2}	0.998		
NH_2_CH_3OH			
C_{CH_3OH}	0.003	0.754	12e
O_{CH_3OH}	0.009		
N_{NH_2}	0.986		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 13 (and Figure S37)

There is no change in the spin density of N before and after interacting with any of the closed shell molecules (Table SI_29). However, substantial local donor-acceptor interactions are revealed through NBO calculations (Table SI_28). AIM analysis gives expected results – namely the confirmation of weak interactions.

Table SI_28: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 13 (main text) and Figure S37 (SI)**. The same level of theory used to optimize the structures in **Figure 13** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 12.78	$N_{NH_2}\cdots H_{HF}$	n (sp) - σ* (sp^3)	0.0463	0.0756	13a
− 9.16	$N_{NH_2}\cdots H_{HCl}$	n (sp) - σ* (s)	0.0341	0.0728	13b
− 3.57	$N_{NH_2}\cdots H_{H_2O}$	n (sp) - σ* (s)	0.0231	0.0717	13c
− 2.08	$N_{NH_2}\cdots H_{H_2S}$	n (sp) - σ* (sp^3)	0.0139	0.0463	13d
− 4.40	$N_{NH_2}\cdots H_{HCN}$	n (sp) - σ* (sp)	0.0183	0.0610	13e
− 9.61	$N_{NH_2}\cdots H_{HNC}$	n (sp) - σ* (sp)	0.0319	0.0790	13f
− 1.52	$N_{NH_2}\cdots H_{HCP}$	n (sp) - σ* (sp)	0.0121	0.0426	S37
Insignificant	$N_{NH_2}\cdots H_{HCP}$	-	0.0109	0.0389	13g
− 4.32	$N_{NH_2}\cdots H_{CH_3OH}$	n (sp) - σ* (sp^3)	0.0238	0.0727	13h

− 0.84	$N_{NH_2}\cdots H_{CH_3SH}$	n (sp) - σ* (s)	0.0097	0.0317	13i

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_29: Spin density for the structures in Figure 13 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
N_{NH_2}	1.000	0.754	
NH_2_HF			
F_{HF}	0.000	0.754	13a
N_{NH_2}	0.999		
NH_2_HCl			
Cl_{HCl}	-0.009	0.754	13b
N_{NH_2}	1.009		
NH_2_H_2O			
O_{H_2O}	-0.005	0.754	13c
N_{NH_2}	1.005		
NH_2_H_2S			
S_{H_2S}	-0.002	0.754	13d
N_{NH_2}	1.002		
NH_2_HCN			
N_{HCN}	0.001	0.754	13e
C_{HCN}	-0.010		
N_{NH_2}	1.009		
NH_2_HNC			
N_{HNC}	-0.006	0.754	13f
C_{HNC}	0.000		
N_{NH_2}	1.006		
NH_2_HCP			
P_{HCP}	0.004	0.754	S37

C_{HCP}	-0.013		
N_{NH_2}	1.008		
NH_2_HCP			
P_{HCP}	0.076	0.755	13g
C_{HCP}	-0.069		
N_{NH_2}	0.993		
NH_2_CH_3OH			
C_{CH_3OH}	0.000	0.754	13h
O_{CH_3OH}	-0.006		
N_{NH_2}	1.005		
NH_2_CH_3SH			
C_{CH_3SH}	-0.000	0.754	13i
S_{CH_3SH}	-0.000		
N_{NH_2}	1.000		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 14 (and Figure S38-S40)

Only 4 modes could be optimized for this mode of interaction. NBO and AIM analysis are given in Table SI_30, and the spin-density calculations in Table SI_31. Electrostatic interactions predominate in all the four optimized structures.

Table SI_30: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 14 (main text) and Figure S38-S40 (SI)**. The same level of theory used to optimize the structures in **Figure 14** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 0.57	$N_{NH_2}\cdots H_{HCl}$	n (p) - σ* (s)	0.0081	0.0319	S38
− 2.40	$N_{NH_2}\cdots P_{HCP}$	n (sp) - σ* (p)	0.0168	0.0442	S39
− 3.02	$N_{NH_2}\cdots P_{PH_3}$	n (p) - σ* (sp^3)	0.0172	0.0467	S40
− 0.91	$N_{NH_2}\cdots S_{CH_3SH}$	n (p) - σ* (sp^3)	0.0109	0.0374	14a

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c.

Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_31: Spin density for the structures in Figure 14 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
N_{NH2}	1.000	0.754	
NH_2_HCl			
Cl_{HCl}	0.001	0.754	S38
N_{NH2}	0.998		
NH_2_HCP			
P_{HCP}	-0.131	0.759	S39
C_{HCP}	0.163		
N_{NH2}	0.967		
NH_2_PH_3			
P_{PH3}	0.026	0.756	S40
N_{NH2}	0.973		
NH_2_CH_3SH			
C_{CH3SH}	-0.000	0.754	14a
S_{CH3SH}	0.001		
N_{NH2}	0.998		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 15 of Main Text

Orbital interaction energies from NBO analysis and AIM analysis **(**Table SI_32**)** confirm the existence of weak interactions here. Moreover, the interactions are electrostatically dominated (indicated by no change in the spin densities – Table SI_33), although the NBO method shows substantial local orbital interactions.

Table SI_32: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 15 (main text)**. The same level of theory used to optimize the structures in **Figure 15** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 2.36	$F_{HF}\cdots H_{HO_2}$	n (p)−σ* (sp^3)	0.0221	0.1045	15a
− 2.35	$Cl_{HCl}\cdots H_{HO_2}$	n (p) - σ* (sp^3)	0.0177	0.0564	15b
− 7.06	$O_{H_2O}\cdots H_{HO_2}$	n (sp^3) - σ* (sp^3)	0.0358	0.1151	15c
− 5.68	$S_{H_2S}\cdots H_{HO_2}$	n (p) - σ* (sp^3)	0.0225	0.0472	15d
− 6.11	$N_{HCN}\cdots H_{HO_2}$	n (sp) - σ* (sp^3)	0.0296	0.0841	15e
− 11.43	$C_{HNC}\cdots H_{HO_2}$	n (sp) - σ* (sp^3)	0.0317	0.0595	15f
− 0.87	$P_{HCP}\cdots H_{HO_2}$	n (sp) - σ* (sp^3)	0.0108	0.0302	15g
Insignificant	$P_{HCP}\cdots H_{HO_2}$	-	0.0208	0.0455	15h
− 19.23	$N_{NH_3}\cdots H_{HO_2}$	n (sp^3) - σ* (sp^3)	0.0553	0.0623	15i
− 5.09	$P_{PH_3}\cdots H_{HO_2}$	n (sp) - σ* (sp^3)	0.0214	0.0419	15j
− 8.16	$O_{CH_3OH}\cdots H_{HO_2}$	n (sp^3) - σ* (sp^3)	0.0149	0.0693	15k
− 8.27	$S_{CH_3SH}\cdots H_{HO_2}$	n (p) - σ* (sp^3)	0.0276	0.0476	15l

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_33: Spin density for the structures in Figure 15 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	**Spin Density**	**$<S^2>$ Value**	**Figure**
O_{HO_2}	0.260	0.755	
O_{HO_2}	0.739		
HO_2_HF			
F_{HF}	-0.002	0.755	15a
O_{HO_2}	0.295		
O_{HO_2}	0.707		
HO_2_HCl			
Cl_{HCl}	-0.002	0.755	15b
O_{HO_2}	0.299		
O_{HO_2}	0.703		

HO_2_H_2O			
O_{H2O}	-0.000	0.755	15c
O_{HO2}	0.282		
O_{HO2}	0.717		
HO_2_H_2S			
S_{H2S}	-0.001	0.755	15d
O_{HO2}	0.269		
O_{HO2}	0.731		
HO_2_HCN			
N_{HCN}	0.000	0.755	15e
C_{HCN}	-0.002		
O_{HO2}	0.279		
O_{HO2}	0.722		
HO_2_HNC			
N_{HNC}	-0.003	0.755	15f
C_{HNC}	0.001		
O_{HO2}	0.291		
O_{HO2}	0.711		
HO_2_HCP			
P_{HCP}	0.000	0.755	15g
C_{HCP}	-0.001		
O_{HO2}	0.271		
O_{HO2}	0.729		
HO_2_HCP			
P_{HCP}	0.000	0.755	15h
C_{HCP}	-0.001		
O_{HO2}	0.287		
O_{HO2}	0.713		
HO_2_NH_3			
N_{NH3}	-0.002	0.755	15i
O_{HO2}	0.267		
O_{HO2}	0.735		
HO_2_PH_3			
P_{PH3}	-0.000	0.755	15j
O_{HO2}	0.264		
O_{HO2}	0.735		
HO_2_CH_3OH			
C_{CH3OH}	-0.004	0.755	15k
O_{CH3OH}	0.002		
O_{HO2}	0.279		
O_{HO2}	0.721		
HO_2_CH_3SH			

C_{CH_3SH}	0.000	0.755	15l
S_{CH_3SH}	-0.001		
O_{HO_2}	0.269		
O_{HO_2}	0.731		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 16 (and Figure S41, S42)

The NBO, AIM and spin density analyses for the structures in Figure 16 (main text) are given in Tables SI_34 and SI_35. Akin to that seen in Tables SI_32 and SI_33, the interactions are electrostatically dominated (indicated by no change in the spin densities – Table SI_35), although the NBO method shows substantial local orbital interactions.

Table SI_34: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 16 (main text) and Figure S41, S42 (SI)**. The same level of theory used to optimize the structures in **Figure 16** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 6.62	$O_{HO_2}\cdots H_{HF}$	n (p)−σ* (sp^3)	0.0344	0.0976	16a
− 4.45	$O_{HO_2}\cdots H_{HCl}$	n (p)−σ* (sp^3)	0.0214	0.0737	16b
− 2.14	$O_{HO_2}\cdots H_{H_2O}$	n (p)−σ* (sp^3)	0.0185	0.0692	16c
− 0.83	$O_{HO_2}\cdots H_{H_2S}$	n (p) - σ* (sp^3)	0.0103	0.0379	16d
− 2.61	$O_{HO_2}\cdots H_{HCN}$	n (p) - σ* (sp)	0.0158	0.0602	16e
− 5.26	$O_{HO_2}\cdots H_{HNC}$	n (p) - σ* (sp)	0.0253	0.0865	16f
− 0.91	$O_{HO_2}\cdots H_{HCP}$	n (p) - σ* (sp)	0.0109	0.0413	16g
Insignificant	$O_{HO_2}\cdots H_{NH_3}$	-	0.0102	0.0396	S41
Insignificant	$O_{HO_2}\cdots H_{PH_3}$	-	0.0068	0.0230	S42
Insignificant	$O_{HO_2}\cdots H_{CH_3OH}$	-	0.0177	0.0675	16h
− 1.00	$O_{HO_2}\cdots S_{CH_3SH}$	n (p) - σ* (sp^3)	0.0099	0.0354	16i

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c. Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_35: Spin density for the structures in Figure 16 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
O_{HO_2}	0.260	0.755	
O_{HO_2}	0.739		
O_2H_HF			
F_{HF}	-0.002	0.755	16a
O_{HO_2}	0.310		
O_{HO_2}	0.691		
O_2H_HCl			
Cl_{HCl}	0.000	0.755	16b
O_{HO_2}	0.271		
O_{HO_2}	0.727		
O_2H_H_2O			
O_{H_2O}	0.000	0.755	16c
O_{HO_2}	0.301		
O_{HO_2}	0.698		
O_2H_H_2S			
S_{H_2S}	-0.001	0.755	16d
O_{HO_2}	0.288		
O_{HO_2}	0.712		
O_2H_HCN			
N_{HCN}	0.001	0.755	16e
C_{HCN}	-0.001		
O_{HO_2}	0.281		
O_{HO_2}	0.719		
O_2H_HNC			
N_{HNC}	-0.001	0.755	16f
C_{HNC}	-0.001		
O_{HO_2}	0.286		
O_{HO_2}	0.716		
O_2H_HCP			
P_{HCP}	0.008	0.755	16g
C_{HCP}	-0.008		
O_{HO_2}	0.269		
O_{HO_2}	0.730		

$O_2H\_NH_3$			
N_{NH3}	0.000	0.755	S41
O_{HO2}	0.305		
O_{HO2}	0.694		
$O_2H\_PH_3$			
P_{PH3}	0.000	0.755	S42
O_{HO2}	0.283		
O_{HO2}	0.715		
$O_2H\_CH_3OH$			
C_{CH3OH}	0.000	0.755	16h
O_{CH3OH}	0.000		
O_{HO2}	0.301		
O_{HO2}	0.697		
$O_2H\_CH_3SH$			
C_{CH3SH}	-0.005	0.755	16i
S_{CH3SH}	0.003		
O_{HO2}	0.288		
O_{HO2}	0.714		

AIM, NBO, and Spin Density Analyses for the Structures in Figure 17 (and Figure S43)

The AIM and NBO analyses for the only two optimized structures obtained are given in Table SI_36. There is no spin-density transfer in both these structures (table SI_37), implying the electrostatic nature of the interactions.

Table SI_36: NBO (columns 1-3) and AIM (columns 4-5) analyses of the structures in **Figure 17 (main text) and Figure S43 (SI)**. The same level of theory used to optimize the structures in **Figure 17** (main text) are used in the NBO calculations, and in the AIM calculations.

Orbital Interaction Energy (kcal/mol)[a]	**Atoms**	**Natural Orbitals Involved[b,c]**	**$\rho(r_c)$[d] (AIM)**	**$\nabla^2\rho(r_c)$[e] (AIM)**	**Figure**
− 2.38	$O_{HO2}\cdots H_{HF}$	n (sp)−σ* (sp^3)	0.0240	0.0892	17a
Insignificant	$O_{HO2}\cdots Cl_{HCl}$	n (sp)−σ* (s)	0.0041	0.0183	S43

a. The orbital interaction energy we report is the negative of the "E(2) stabilization energy" arising due to the interaction between the donor and acceptor natural orbitals. By "insignificant", we refer to the any E(2) value being less than 0.50 kcal/mol. The results from alpha spin orbitals are presented here. The NBO results from the beta spin orbitals are very similar. c.

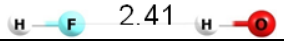
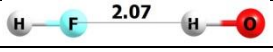
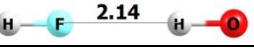
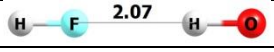
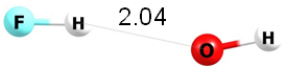
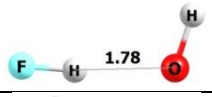
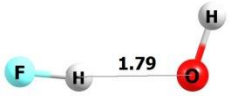
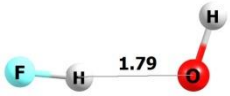
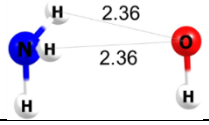
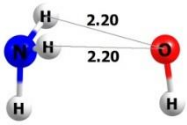
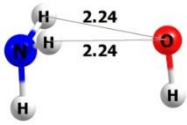
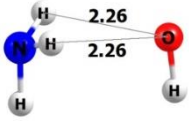
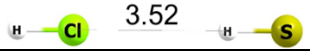
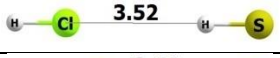
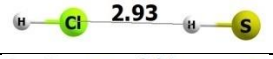
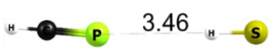
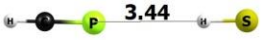
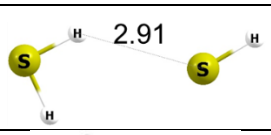
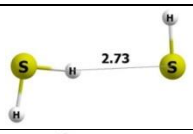
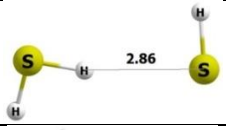
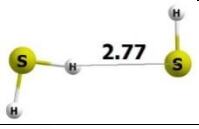
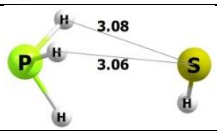
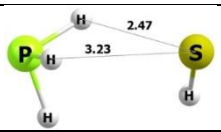
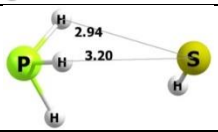
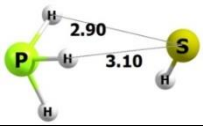
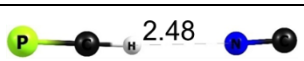
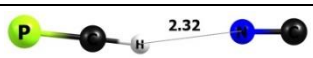
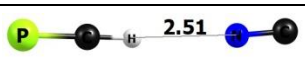
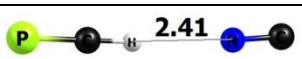
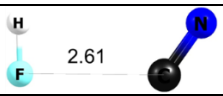
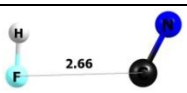
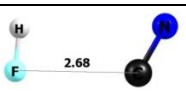
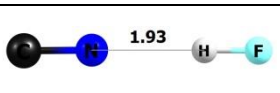
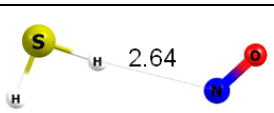
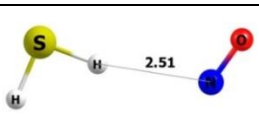
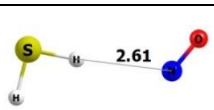
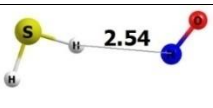
Hybridizations are obtained after rounding-off the percent "s" and "p" character to the closest integer. d. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ in a.u.

Table SI_37: Spin density for the structures in Figure 17 (main text). UM06-2x/aug-cc-pVTZ level of theory. The $<S^2>$ values are given side-by-side (3rd column) so that it is clear that, the transfer in spin-density is not an artefact of spin-contamination. The figures where the structures can be found in the main text are given in the 4th column.

Atoms	Spin Density	$<S^2>$ Value	Figure
O_{HO_2}	0.260	0.755	
O_{HO_2}	0.739		
HO_2_HF			
F_{HF}	0.001	0.755	17a
O_{HO_2}	0.236		
O_{HO_2}	0.762		
HO_2_HCl			
Cl_{HCl}	0.000	0.755	S43
O_{HO_2}	0.260		
O_{HO_2}	0.739		

Table SI_38: Method Calibration – Geometries

In the main text the UM06-2x/aug-cc-pVTZ was used for optimization. Here, we demonstrate for representative cases that even with several other density functionals, similar geometries of the complexes are mostly obtained. Other methods chosen - UB3-LYP(D3-BJ)/aug-cc-pVTZ (3rd column), UB2PLYP(D3-BJ)/aug-cc-pVTZ (5th column), and UωB97X-D/aug-cc-pVTZ (4th column). The geometries in the 2nd column are the ones from the main text.

Systems	UM06-2x	UB3LYP(D3-BJ)	UωB97X-D	UB2PLYP(D3-BJ)
OH···Molecules				
In Figure 1				
OH···HF				
In Figure 2				
OH···HF				
OH···NH_3				
SH···Molecules				
In Figure 3				
SH···HCl				
SH···HCP				
In Figure 4				
SH···H_2S				
SH···PH_3				
CN···Molecules				
In Figure 6				
CN···HCP				
In Figure 8				
CN···HF				
NO···Molecules				
In Figure 9				
NO···H_2S				

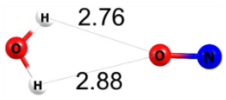
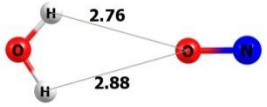
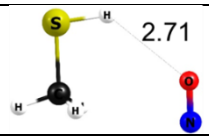
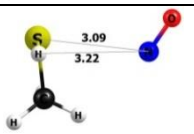
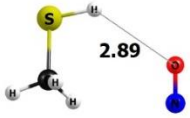
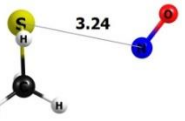
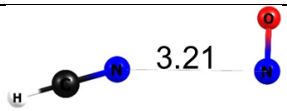
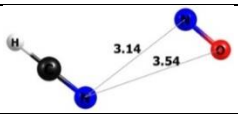
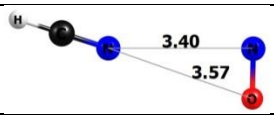
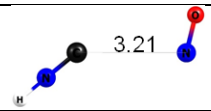
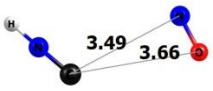
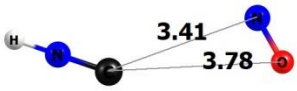
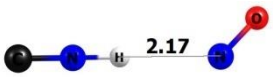
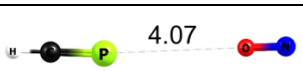
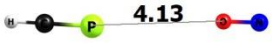
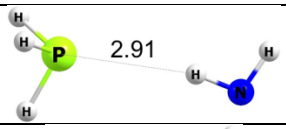
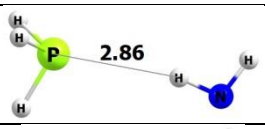
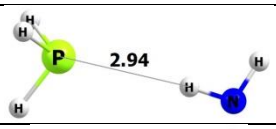
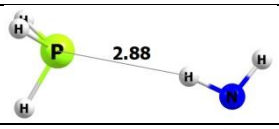
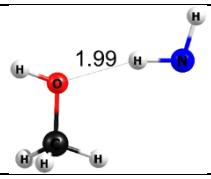
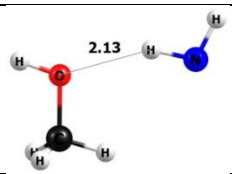
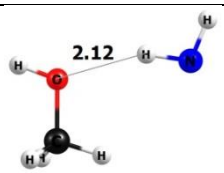
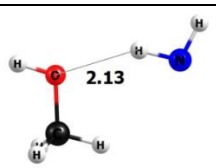
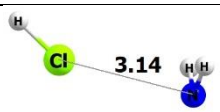
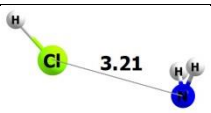
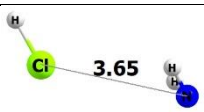
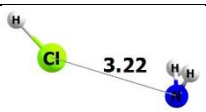
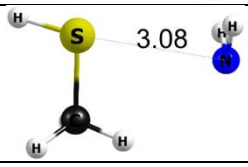
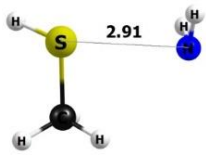
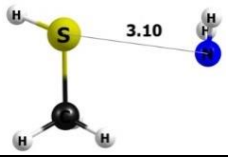
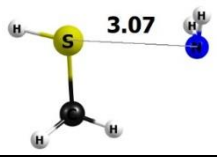
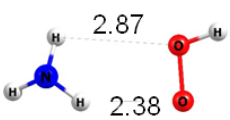
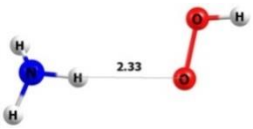
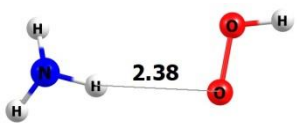
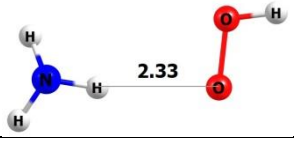
In Figure 10				
NO···H_2O				
NO···CH_3SH				
In Figure 11				
NO···HCN				
NO···HNC				
In Figure S34				
NO···HCP				
NH_2···Molecules				
In Figure 12				
NH_2···PH_3				
NH_2···CH_3OH				
In Figure 14				
NH_2···HCl				
NH_2···CH_3SH				
HO_2···Molecules				
In Figure 16				
HO_2···NH_3				

Table SI_39: Method Calibration – Interaction energies

The interaction energy in the main text was computed at the (CCSD(T)(FC)/aug-cc-pVTZ//UM06-2x/aug-cc-pVTZ) level of theory. Here, we demonstrate for representative cases that even with geometries obtained using several other density functionals, the interaction energies don't change much. Level of theory used to compare the interaction energies: UCCSD(T)(FC)/aug-cc-pVTZ//UB3-LYP(D3-BJ)/aug-cc-pVTZ (3rd column), UCCSD(T)(FC)/aug-cc-pVTZ//UB2PLYP(D3-BJ)/aug-cc-pVTZ (5th column), and UCCSD(T)(FC)/aug-cc-pVTZ//UωB97X-D/aug-cc-pVTZ (4th column). All the energies include zero point and BSSE corrections. The interaction energies in the 2nd column are the ones from the main text.

Systems	**CCSD(T) /M06-2x**	**CCSD(T)/ B3LYP**	**CCSD(T)/ ωB97X-D**	**CCSD(T)/ B2PLYP**
OH···Molecules				
In Figure 1				
OH···HF	−1.33	−1.60	−1.65	−1.09
In Figure 2				
OH···HF	−2.96	−3.70	−3.65	−3.71
OH···NH_3	0.61	1.69	1.49	0.76
SH···Molecules				
In Figure 3				
SH···HCl	1.42	−0.10	−0.03	−0.13
SH···HCP	0.35	−0.08	−0.06	−0.01
In Figure 4				
SH···H_2S	0.48	−0.69	−0.75	−0.67
SH···PH_3	1.63	0.59	0.03	−0.22
CN···Molecules				
In Figure 6				
CN···HCP	0.13	0.14	−0.91	−0.22
In Figure 8				
CN···HF	0.16	−0.36	−0.37	−2.20
NO···Molecules				
In Figure 9				
NO···H_2S	0.57	−0.17	−0.18	−0.31
In Figure 10				
NO···H_2O	0.00	−0.12	−0.21	−0.15
NO···CH_3SH	0.19	−0.32	−0.32	−0.72
In Figure 11				
NO···HCN	0.30	0.24	0.12	−0.68

NO··· HNC	0.65	−0.09	0.23	−1.28
In Figure S34				
NO···HCP	0.10	−0.10	−0.13	−0.12
NH_2···Molecules				
In Figure 12				
NH_2···PH_3	−0.12	−0.51	−0.27	−0.08
NH_2···CH_3OH	−2.03	−2.07	−1.86	−2.08
In Figure 14				
NH_2···HCl	0.43	0.16	0.13	0.04
NH_2···CH_3SH	−0.10	−0.06	−0.78	−1.02
HO_2···Molecules				
In Figure 16				
HO_2···NH_3	0.40	−0.58	−0.47	−0.57

Table SI_40: Interaction Energies using Complete Basis-Set Extrapolation

To be certain that the triple-ζ quality basis-set used is appropriate, we calculate energies at the UCCSD(T) (FC)/aug-cc-pVQZ level of theory using much larger quadruple-ζ basis-set (starting with UM06-2x/aug-cc-pVTZ geometries). Also, we employ two different two-point complete-basis set (CBS) extrapolation scheme – one wherein we extrapolate only the correlation energy, and another wherein we extrapolate both the Hartree-Fock energy and the correlation energy; to get the UCCSD(T)(FC) energies at the infinite basis-set limit.

In the following table, CBS 1 (4^{th} column) refers to the interaction energies obtained via a complete basis-set extrapolation scheme wherein we only extrapolate the correlation energies and then add them to the HF/Aug-cc-pVQZ energies. The correlation energies (in Hartree) were themselves extrapolated using the following formula adapted from reference 159 in the main text:

$$E(Corr)_{CBS} = -(27\ E_{corr\text{-}TZ} - 64\ E_{corr\text{-}QZ})/37$$

Similarly, CBS 2 (5^{th} column) (refers to refers to the interaction energies obtained via a complete basis-set extrapolation scheme wherein we add $E(Corr)_{CBS}$ to $E(HF)_{CBS}$, and $E(HF)_{CBS}$ in Hartrees is obtained using the following formula adapted from reference 160 in the main text using the α value 1.63:

$$E(HF)_{CBS} = \{(e^{-4\alpha} - e^{-3\alpha})/e^{-7\alpha}\}^{-1}\{(E_{HF\text{-}QZ}/\ e^{-4\alpha}) - (E_{HF\text{-}TZ}/\ e^{-3\alpha})\}$$

aug-cc-pVTZ (2^{nd} column) and aug-cc-pVQZ (3^{rd} column) refer to the interaction energies obtained using the two different basis sets, respectively. The interaction energies computed using all the 4 methods (aug-cc-pVTZ, aug-cc-pVQZ, CBS 1, and CBS 2) include zero point corrections from the UM06-2x/aug-cc-pVTZ geometries

Systems	aug-cc-pVTZ	aug-cc-pVQZ	CBS 1	CBS 2
OH···Molecules				
In Figure 1				
OH···HF	−1.33	−1.39	−1.42	−1.41
In Figure 2				
OH···HF	−2.96	−3.09	−3.15	−3.15
OH···NH_3	0.61	0.36	0.21	0.22
SH···Molecules				
In Figure 3				
SH···HCl	1.42	1.42	1.38	1.39
SH···HCP	0.35	0.21	0.30	0.31
In Figure 4				
SH···H_2S	0.48	0.46	0.31	0.32
SH···PH_3	1.63	1.56	1.31	1.34

CN···Molecules				
In Figure 6				
CN···HCP	0.13	−0.09	−0.33	−0.27
In Figure 8				
CN···HF	0.16	0.03	−0.10	−0.08
NO···Molecules				
In Figure 9				
NO···H_2S	0.57	0.56	0.47	0.48
In Figure 10				
NO···H_2O	0.00	−0.05	−0.10	−0.08
NO···CH_3SH	0.19	0.12	−0.03	0.00
In Figure 11				
NO···HCN	0.30	0.22	0.18	0.19
NO··· HNC	0.65	0.55	0.53	0.54
In Figure S34				
NO···HCP	0.10	−0.06	0.07	0.08
NH_2···Molecules				
In Figure 12				
NH_2···PH_3	−0.12	−0.10	−0.18	−0.16
NH_2···CH_3OH	−2.03	−2.23	−2.36	−2.34
In Figure 14				
NH_2···HCl	0.43	0.33	0.26	0.26
NH_2···CH_3SH	−0.10	−0.14	−0.32	−0.31
HO_2···Molecules				
In Figure 16				
HO_2···NH_3	0.40	0.34	0.30	0.33

Co-ordinates of the Optimized Geometries (UM06-2x/augg-cc-pVTZ)

All geometries correspond to doublet spin states, are neutral, and do not have any imaginary frequencies. The magnitude of the lowest vibrational frequency (harmonic, in cm^{-1}) in each of the structures is given below the corresponding co-ordinates.

Figure 1 from main-text

a)

O	0.000000000	0.000000000	1.880119000
H	0.000000000	0.000000000	0.906742000
H	0.000000000	0.000000000	-2.424094000
F	0.000000000	0.000000000	-1.502622000

27.95 cm^{-1}

b)

O	0.000796000	1.930623000	0.000000000
H	0.960801000	1.777718000	0.000000000
H	-0.980691000	-0.177589000	0.000000000
Cl	0.000796000	-1.002653000	0.000000000

125.52 cm^{-1}

c)

O	1.636178000	-0.000058000	0.000030000
H	0.648040000	-0.001129000	0.000730000
N	-1.262088000	-0.000161000	-0.000102000
H	-1.636235000	-0.122869000	0.932871000
H	-1.635876000	-0.746227000	-0.573619000
H	-1.630731000	0.871821000	-0.359510000

205.49 cm^{-1}

d)

O	-1.613973000	0.000015000	0.015105000
H	-0.637652000	-0.004546000	-0.057565000
O	1.258765000	-0.000881000	-0.069755000
H	1.748649000	-0.761830000	0.249723000
H	1.730667000	0.773308000	0.245040000

158.15 cm^{-1}

e)

O	2.346782000	-0.000008000	0.017099000
H	1.380899000	-0.000031000	-0.129915000
S	-1.109592000	-0.000003000	-0.102668000
H	-1.200674000	0.968858000	0.817835000
H	-1.201003000	-0.968707000	0.817972000

117.53 cm^{-1}

f)

O	2.493254000	0.000299000	-0.000192000
H	1.516396000	-0.009056000	0.004182000
H	-1.788788000	1.210767000	-0.021611000
H	-1.830405000	-0.573017000	1.041981000
H	-1.815872000	-0.602651000	-1.034259000
P	-1.068491000	-0.001896000	0.000749000

119.17 cm^{-1}

g)

O	0.000000000	0.000000000	2.281971000
H	0.000000000	0.000000000	1.305086000
H	0.000000000	0.000000000	-2.958079000
N	0.000000000	0.000000000	-0.750926000
C	0.000000000	0.000000000	-1.891049000

78.68 cm^{-1}

h)

O	0.000000000	0.000000000	2.397645000
H	0.000000000	0.000000000	1.419269000
H	0.000000000	0.000000000	-2.894998000
N	0.000000000	0.000000000	-1.896175000
C	0.000000000	0.000000000	-0.738701000

71.63 cm^{-1}

i)

O	2.537960000	-0.192909000	-0.001345000
H	1.563863000	-0.146467000	0.014783000
H	-0.072379000	1.927401000	-0.000373000
C	-0.545304000	0.964790000	-0.000080000
P	-1.234889000	-0.401760000	-0.000211000

48.85 cm^{-1}

j)

O	-2.144605000	-0.185837000	0.000307000
H	-1.265481000	0.247378000	-0.000163000
C	1.381178000	-0.496539000	0.000279000
H	0.724910000	-1.363315000	-0.001775000
H	2.011596000	-0.528619000	-0.889316000
H	2.006741000	-0.529435000	0.893256000
O	0.540423000	0.648886000	-0.001659000
H	1.068614000	1.448834000	0.007132000

54.37 cm^{-1}

k)

O	1.613739000	0.499616000	0.055566000
H	2.216018000	-0.095515000	-0.409500000
C	-1.119270000	0.864392000	0.001115000
H	-1.187245000	1.220774000	-1.022659000
H	-2.114271000	0.749116000	0.420352000
H	-0.508354000	1.548681000	0.579945000
H	-0.147717000	-0.928410000	1.237662000
S	-0.278295000	-0.729870000	-0.078564000

133.41 cm^{-1}

Figure 2 from main-text

a)

O	0.023918000	1.456036000	0.000000000
H	-0.309638000	2.370607000	0.000000000
H	-0.096963000	-0.576561000	0.000000000
F	0.023918000	-1.493592000	0.000000000

61.21 cm^{-1}

b)

O	0.000200000	2.181432000	0.000000000
H	-0.006648000	3.153343000	0.000000000
H	0.001638000	0.067364000	0.000000000
Cl	0.000200000	-1.216009000	0.000000000

113.78 cm^{-1}

c)

O	-2.384854000	0.110551000	-0.019780000
H	-2.684928000	-0.784035000	0.215865000
S	1.259455000	-0.095005000	-0.005285000
H	-0.027995000	0.245983000	-0.158542000
H	1.640468000	1.173727000	0.185481000

48.50 cm^{-1}

d)

O	2.258432000	-0.085796000	-0.000043000
H	2.854909000	0.682580000	0.000049000
C	-1.000542000	-0.029393000	0.000113000

H	0.069019000	-0.085658000	0.000231000
N	-2.141162000	0.037972000	-0.000087000

67.62 cm^{-1}

e)

O	-2.037259000	-0.091390000	-0.000334000
H	-2.503786000	0.762871000	0.000391000
H	-0.088074000	-0.098474000	0.001465000
N	0.918683000	-0.033727000	0.000746000
C	2.076525000	0.050469000	-0.000734000

116.52 cm^{-1}

f)

O	2.199411000	-0.177037000	-0.000001000
H	1.799042000	-1.061972000	0.000005000
C	-0.221588000	0.858817000	0.000001000
H	0.471915000	1.676005000	0.000000000
P	-1.235781000	-0.290043000	0.000000000

61.72 cm^{-1}

Figure 3 from main-text

a)

S	0.000000000	0.000000000	1.440951000
H	0.000000000	0.000000000	0.097801000
H	0.000000000	0.000000000	-3.143861000
F	0.000000000	0.000000000	-2.223240000

75.12 cm^{-1}

b)

S	1.398528000	0.000000000	0.002100000
H	0.052038000	-0.000020000	-0.004416000
O	-2.129858000	-0.000008000	-0.027746000
H	-2.694875000	-0.765475000	0.096400000
H	-2.694740000	0.765561000	0.096387000

109.92 cm^{-1}

c)

S	-2.118504000	0.000009000	0.014114000
H	-0.839149000	0.000567000	-0.400669000
H	1.824562000	0.968076000	0.825607000
H	1.822270000	-0.967757000	0.825745000
S	1.943024000	-0.000065000	-0.092282000

64.33 cm^{-1}

d)

S	0.000000000	0.000000000	2.024631000
H	0.000000000	0.000000000	0.679580000
C	0.000000000	0.000000000	-2.856828000
H	0.000000000	0.000000000	-3.923541000
N	0.000000000	0.000000000	-1.715596000

66.36 cm^{-1}

e)

S	0.000000000	0.000000000	2.112897000
H	0.000000000	0.000000000	0.766675000
H	0.000000000	0.000000000	-3.893531000
N	0.000000000	0.000000000	-2.895095000
C	0.000000000	0.000000000	-1.735640000

50.51 cm^{-1}

f)

S	2.396807000	-0.080631000	-0.000021000
H	1.052496000	-0.107153000	0.000487000
C	-1.355250000	0.957445000	-0.000020000
H	-0.889017000	1.922865000	0.000054000
P	-2.025393000	-0.418020000	-0.000006000

50.89 cm^{-1}

g)

S	1.948475000	-0.037363000	0.000006000
H	1.481883000	-1.295282000	-0.000086000
C	-1.027099000	0.970153000	-0.000005000
H	-0.554249000	1.931926000	-0.000028000
P	-1.729376000	-0.390650000	0.000004000

67.33 cm^{-1}

h)

S	-1.411329000	0.000021000	-0.000005000
H	-0.058000000	0.000128000	0.000113000
N	2.151999000	0.000241000	-0.000006000
H	2.524265000	-0.482231000	-0.808439000
H	2.524288000	-0.460564000	0.820940000
H	2.526712000	0.940640000	-0.012501000

123.05 cm^{-1}

i)

S	-2.288395000	-0.000022000	-0.000261000
H	-0.942852000	0.001512000	-0.013537000
H	2.759265000	1.078949000	-0.450659000
H	2.766389000	-0.982372000	-0.625419000
H	2.611431000	-0.103302000	1.239873000
P	1.961339000	0.000371000	-0.009739000

63.57 cm^{-1}

j)

S	1.896843000	-0.064429000	0.002246000
H	0.703759000	0.560582000	-0.007032000
C	-1.918270000	-0.612168000	0.003378000
H	-1.069062000	-1.272683000	-0.158507000
H	-2.368341000	-0.851720000	0.968830000
H	-2.650528000	-0.780872000	-0.788442000
O	-1.415354000	0.714488000	-0.024491000
H	-2.132867000	1.332660000	0.124882000

35.11 cm^{-1}

k)

S	2.196772000	-0.073503000	0.005944000
H	1.157995000	-0.928284000	0.004468000
C	-1.017022000	1.170389000	0.008694000
H	-0.573522000	1.393430000	-0.958955000
H	-1.840972000	1.854072000	0.189369000
H	-0.257492000	1.282588000	0.778632000
H	-1.947804000	-0.674546000	1.201375000
S	-1.599026000	-0.548347000	-0.085135000

53.75 cm^{-1}

Figure 4 from main-text

a)

S	0.047351000	-1.160651000	0.000000000
H	-1.296270000	-1.169749000	0.000000000
H	0.112504000	1.138910000	0.000000000
F	0.047351000	2.066805000	0.000000000

147.73 cm^{-1}

b)

S	-1.911536000	-0.074544000	-0.000181000
H	-1.837174000	1.266206000	0.000611000
H	0.591107000	-0.143559000	0.006761000
Cl	1.872391000	0.004121000	-0.000264000

91.66 cm^{-1}

c)

S	-1.270365000	-0.074320000	-0.001889000
H	-0.994635000	1.239387000	0.052623000
O	2.166894000	0.105394000	-0.012325000
H	1.262050000	-0.224534000	-0.013749000
H	2.723269000	-0.668875000	0.089945000

6.45 cm^{-1}

d)

S	-1.932706000	-0.079650000	-0.000146000
H	-2.152542000	1.245706000	0.000023000
C	1.867928000	-0.009210000	0.000984000
H	0.796928000	-0.031128000	0.002131000
N	3.010192000	0.016441000	-0.000817000

87.02 cm^{-1}

e)

S	-1.765112000	-0.074757000	-0.000275000
H	-1.853362000	1.265273000	0.000471000
H	0.718239000	-0.085714000	0.001734000
N	1.724774000	-0.030510000	0.001786000
C	2.883917000	0.038354000	-0.001717000

101.40 cm^{-1}

f)

S	-2.801760000	-0.060408000	-0.013831000
H	-2.717055000	1.281452000	0.056457000
C	1.172132000	-0.114644000	0.065389000
H	0.103973000	-0.222174000	0.121103000
P	2.693896000	0.039674000	-0.023240000

51.35 cm^{-1}

g)

S	-1.723326000	-0.106954000	-0.033227000
H	-2.485181000	0.876638000	0.470977000
C	1.809352000	-0.598236000	0.034993000
H	2.881176000	-0.769388000	0.109056000
H	1.329057000	-1.042251000	0.912307000
H	1.440307000	-1.104788000	-0.861617000
O	1.610828000	0.797676000	-0.027198000
H	0.665124000	0.959059000	-0.091460000

63.76 cm^{-1}

h)

S	-1.762421000	0.183623000	0.057597000
H	-1.977380000	-0.685055000	-0.940004000
C	1.538894000	1.000910000	-0.029623000
H	1.508741000	1.345362000	-1.059561000
H	0.874756000	1.617221000	0.567952000
H	2.557882000	1.045523000	0.342418000
S	0.944098000	-0.710371000	-0.057604000
H	0.895801000	-0.900534000	1.267034000

85.57 cm^{-1}

Figure 5 from main-text

a)

S	1.095224000	-0.070993000	-0.000396000
H	0.803143000	1.237200000	-0.003819000
H	-1.869275000	-0.464348000	0.771279000
H	-1.907809000	-0.479016000	-0.757403000
O	-1.818705000	0.105257000	-0.000465000

91.73 cm^{-1}

b)

S	1.541927000	-0.129303000	-0.002593000
H	1.317191000	1.190840000	0.062332000
C	-2.147067000	-0.337709000	0.005509000
H	-2.772902000	-1.201388000	0.020593000
N	-1.476103000	0.586522000	-0.010641000

74.93 cm^{-1}

c)

S	-1.573152000	-0.130601000	-0.000042000
H	-1.574673000	1.209750000	0.001379000
H	3.076791000	-0.754551000	0.000941000
N	2.260360000	-0.179625000	0.000055000
C	1.307632000	0.481964000	-0.000338000

57.81 cm^{-1}

d)

S	1.289867000	-0.273255000	-0.000011000
H	1.882788000	0.928859000	0.000256000
C	-1.637089000	-0.706027000	-0.000004000
H	-2.651771000	-1.058977000	0.000165000
P	-0.669758000	0.582557000	-0.000015000

257.44 cm^{-1}

e)

S	1.336894000	0.072401000	0.003693000
H	1.424150000	-1.251673000	-0.177761000
H	-1.284091000	1.347159000	-0.118006000
H	-1.425184000	-0.192467000	1.331637000
H	-2.508522000	-0.332689000	-0.476210000
P	-1.173111000	-0.048583000	-0.041250000

181.56 cm^{-1}

f)

S	1.578606000	-0.137997000	-0.044506000
H	1.551614000	0.888556000	0.816047000
C	-1.797890000	-0.516032000	0.034776000
H	-1.737204000	-0.914761000	1.044022000
H	-2.848798000	-0.402985000	-0.238336000
H	-1.320455000	-1.224366000	-0.645691000
O	-1.126191000	0.733536000	0.046508000
H	-1.105978000	1.089412000	-0.844674000

8.68 cm^{-1}

Figure 6 from main-text

a)

C	-0.002584000	2.040509000	0.000000000
N	0.000000000	0.892659000	0.000000000
F	0.001597000	-1.942020000	0.000000000
H	0.001127000	-1.013485000	0.000000000

95.13 cm^{-1}

b)

C	0.000000000	0.000000000	-2.883842000
N	0.000000000	0.000000000	-1.734100000
Cl	0.000000000	0.000000000	1.707069000
H	0.000000000	0.000000000	0.421569000

78.85 cm^{-1}

c)

N	0.000000000	1.039606000	0.000000000
C	-0.261181000	2.159599000	0.000000000
O	0.061694000	-2.090891000	0.000000000
H	0.976327000	-2.378357000	0.000000000
H	0.097210000	-1.129347000	0.000000000

82.34 cm^{-1}

d)

N	1.333497000	-1.432662000	0.000000000
C	1.609596000	-2.550471000	0.000000000
S	-1.153704000	1.379321000	0.000000000
H	0.000000000	0.697578000	0.000000000
H	-0.532797000	2.564756000	0.000000000

58.59 cm^{-1}

e)

C	0.000000000	0.000000000	1.614466000
H	0.000000000	0.000000000	0.544255000
N	0.000000000	0.000000000	2.756966000
N	0.000000000	0.000000000	-1.740808000
C	0.000000000	0.000000000	-2.890692000

62.28 cm^{-1}

f)

N	0.000000000	0.000000000	-1.505157000
H	0.000000000	0.000000000	-0.498258000
C	0.000000000	0.000000000	-2.665795000
N	0.000000000	0.000000000	1.549071000
C	0.000000000	0.000000000	2.697605000

69.29 cm^{-1}

g)

N	-1.205539000	0.000015000	0.144118000
C	-2.326715000	-0.000013000	-0.117767000
N	2.267986000	-0.000006000	-0.139402000
H	1.263230000	-0.000001000	-0.010059000
H	2.629968000	0.813359000	0.341800000
H	2.629966000	-0.813346000	0.341842000

69.33 cm^{-1}

h)

N	-2.293176000	0.001224000	0.133070000
C	-3.417865000	-0.001117000	-0.116773000
P	2.072603000	-0.000579000	-0.133105000
H	0.698891000	-0.010255000	0.197527000
H	2.376588000	1.037122000	0.777079000
H	2.394895000	-1.020046000	0.791120000

29.43 cm^{-1}

i)

N	1.592165000	-0.184247000	0.013284000
C	2.656795000	0.250564000	-0.011772000
O	-1.437103000	-0.762938000	-0.006200000
H	-0.488691000	-0.914840000	0.011309000
C	-1.651972000	0.631844000	0.001310000
H	-2.727414000	0.793973000	-0.031058000
H	-1.258572000	1.100586000	0.907738000
H	-1.202593000	1.119058000	-0.868603000

37.94 cm^{-1}

Figure 7 from main-text

a)

C	2.739801000	0.368460000	-0.000043000
H	3.710681000	0.821235000	0.000224000
P	1.349925000	-0.270156000	-0.000044000
C	-3.724273000	0.145899000	-0.000371000
N	-2.578960000	0.020707000	0.000416000

25.76 cm^{-1}

b)

C	2.030961000	-0.000183000	-0.148570000
N	0.898400000	0.000222000	0.159172000
P	-0.929786000	-0.000047000	-0.071310000
H	-1.129403000	-1.097880000	0.763189000
H	-2.268377000	-0.000983000	-0.677624000
H	-1.129993000	1.099118000	0.761304000

124.65 cm^{-1}

c)

H	-0.772244000	-1.062622000	1.127768000
N	1.401054000	-0.004478000	0.446320000
C	2.190234000	0.343130000	-0.358918000
C	-1.258347000	1.004825000	0.031880000
H	-1.052721000	1.499568000	-0.912855000
H	-2.326653000	0.992533000	0.229136000
H	-0.701747000	1.487170000	0.827945000
S	-0.659083000	-0.685815000	-0.152125000

57.90 cm^{-1}

Figure 8 from main text

a)

O	1.556604000	-0.035341000	-0.039414000

H	1.496510000	0.820240000	-0.478934000
H	1.620058000	0.160625000	0.901873000
C	-0.668669000	-0.373290000	-0.073161000
N	-1.651055000	0.220229000	0.047335000

99.02 cm^{-1}

b)

C	1.111065000	-0.358317000	-0.022152000
N	2.126313000	0.195873000	0.007588000
S	-1.208443000	0.037118000	-0.097122000
H	-0.898971000	1.040329000	0.737015000
H	-1.316516000	-0.855425000	0.896732000

67.01 cm^{-1}

c)

C	0.000000000	0.000000000	-2.412050000
H	0.000000000	0.000000000	-3.479193000
N	0.000000000	0.000000000	-1.271248000
N	0.000000000	0.000000000	2.597109000
C	0.000000000	0.000000000	1.445078000

17.65 cm^{-1}

d)

N	1.521914000	0.251619000	-0.000103000
C	0.602745000	-0.458575000	-0.000116000
N	-1.348819000	0.071765000	-0.000562000
H	-1.314774000	1.013880000	-0.364355000
H	-1.649623000	0.036869000	0.963063000
H	-1.863739000	-0.562983000	-0.593356000

46.60 cm^{-1}

e)

O	-0.885707000	-0.720303000	-0.092348000
H	-0.944998000	-1.156259000	0.764816000
C	1.216911000	-0.447032000	-0.069681000
N	1.950753000	0.438786000	0.047428000
C	-1.395104000	0.615258000	0.005288000
H	-1.202022000	1.087102000	-0.952579000
H	-2.467985000	0.579604000	0.191252000
H	-0.885455000	1.171118000	0.789657000

69.38 cm^{-1}

f)

H	-0.847880000	-0.928511000	1.210729000

C	1.434541000	-0.493103000	0.044348000
N	2.172954000	0.397460000	-0.027695000
C	-1.009773000	1.154310000	0.032207000
H	-0.867919000	1.536050000	-0.974728000
H	-1.999301000	1.411376000	0.397663000
H	-0.221051000	1.531249000	0.674290000
S	-0.863946000	-0.643726000	-0.098338000

53.14 cm^{-1}

Figure 9 from main text

a)

O	1.065355000	1.364609000	0.000000000
N	0.000000000	0.978113000	0.000000000
F	-0.877389000	-1.865417000	0.000000000
H	-0.626338000	-0.974910000	0.000000000

75.84 cm^{-1}

b)

O	0.576527000	-2.395534000	0.000000000
N	1.123109000	-1.401241000	0.000000000
Cl	-0.733763000	1.668097000	0.000000000
H	0.000000000	0.615314000	0.000000000

52.23 cm^{-1}

c)

N	0.000000000	1.241343000	0.000000000
O	1.127354000	1.111036000	0.000000000
O	-0.797798000	-1.809235000	0.000000000
H	-1.655664000	-2.237893000	0.000000000
H	-0.980782000	-0.865924000	0.000000000

31.36 cm^{-1}

d)

C	-0.293004000	1.806507000	0.000000000
H	0.000000000	0.779020000	0.000000000
N	-0.607429000	2.904795000	0.000000000
N	0.692610000	-1.599910000	0.000000000
O	0.145220000	-2.594032000	0.000000000

58.19 cm^{-1}

e)

N	-0.317229000	1.656949000	0.000000000

H	0.000000000	0.705392000	0.000000000
C	-0.683817000	2.758945000	0.000000000
N	0.718539000	-1.397054000	0.000000000
O	0.161717000	-2.384791000	0.000000000

65.47 cm^{-1}

f)

C	-1.070785000	0.276600000	0.000000000
H	0.000000000	0.222136000	0.000000000
N	2.654722000	-0.002626000	0.000000000
O	3.351643000	-0.899665000	0.000000000
P	-2.598099000	0.355598000	0.000000000

30.71 cm^{-1}

g)

N	1.547852000	-0.601419000	-0.000077000
O	2.012979000	0.434260000	-0.000202000
O	-1.668719000	-0.693628000	-0.000126000
H	-0.821308000	-1.143889000	0.001267000
C	-1.432745000	0.699406000	0.000186000
H	-2.404044000	1.188888000	0.000285000
H	-0.883611000	1.021542000	0.889390000
H	-0.883604000	1.021899000	-0.888890000

58.54 cm^{-1}

h)

N	-2.030515000	-0.715803000	0.002170000
O	-2.582003000	0.277873000	-0.001469000
C	0.772743000	1.109504000	0.000961000
H	1.497566000	1.919281000	-0.000233000
H	0.155923000	1.188254000	-0.889442000
H	0.159018000	1.188130000	0.893517000
S	1.733297000	-0.431071000	-0.000837000
H	0.687915000	-1.267925000	0.000355000

33.53 cm^{-1}

Figure 10 from main text

a)

N	1.086399000	1.357379000	0.000000000
O	0.000000000	1.017029000	0.000000000
F	-0.777968000	-1.854376000	0.000000000
H	-0.603079000	-0.948504000	0.000000000

47.97 cm^{-1}

b)

N	0.972797000	-2.163482000	0.000000000
O	1.464354000	-1.137433000	0.000000000
Cl	-1.089671000	1.384233000	0.000000000
H	0.000000000	0.711885000	0.000000000

41.02 cm^{-1}

c)

C	-0.243616000	1.782035000	0.000000000
H	0.000000000	0.743008000	0.000000000
N	-0.505207000	2.893964000	0.000000000
O	0.603374000	-1.655749000	0.000000000
N	0.024450000	-2.635282000	0.000000000

43.78 cm^{-1}

d)

N	-0.302023000	1.621479000	0.000000000
H	0.000000000	0.667357000	0.000000000
C	-0.649025000	2.729859000	0.000000000
O	0.684177000	-1.443986000	0.000000000
N	0.076414000	-2.406425000	0.000000000

36.23 cm^{-1}

e)

C	-0.435106000	1.087689000	0.000000000
H	0.000000000	0.108660000	0.000000000
P	-1.062089000	2.482624000	0.000000000
O	1.156407000	-2.400250000	0.000000000
N	1.327244000	-3.524593000	0.000000000

27.25 cm^{-1}

f)

O	-1.573094000	-0.535304000	0.000007000
N	-1.990589000	0.522806000	-0.000188000
O	1.624864000	-0.704344000	-0.000805000
H	0.768606000	-1.136013000	0.004744000
C	1.427170000	0.695242000	0.000256000
H	2.412282000	1.156203000	-0.000475000
H	0.887151000	1.033456000	-0.888358000
H	0.888906000	1.032438000	0.890251000

58.31 cm^{-1}

Figure 11 from main text

a)

N	0.918518000	0.562474000	0.003419000
O	1.518530000	-0.402796000	-0.002109000
H	-1.897177000	0.417968000	-0.747575000
H	-1.907456000	0.368008000	0.775953000
O	-1.846654000	-0.187615000	-0.004430000

47.72 cm^{-1}

b)

N	1.015174000	0.565420000	0.000207000
O	1.567415000	-0.428713000	-0.000348000
N	-1.858834000	-0.089491000	-0.000493000
H	-1.903791000	0.921453000	-0.029574000
H	-2.351803000	-0.387641000	0.831657000
H	-2.378106000	-0.435613000	-0.797301000

32.22 cm^{-1}

c)

N	1.426118000	-0.551765000	0.225253000
O	2.116871000	0.257796000	-0.173961000
O	-1.049724000	0.706069000	0.046828000
H	-1.606478000	1.407619000	0.388544000
C	-1.817878000	-0.475789000	-0.090733000
H	-1.143751000	-1.246947000	-0.456285000
H	-2.233968000	-0.804149000	0.864441000
H	-2.628530000	-0.350363000	-0.812017000

51.10 cm^{-1}

d)

N	-1.902924000	0.578732000	-0.219210000
O	-2.545821000	-0.276100000	0.163764000
H	2.273110000	-1.224835000	-0.184073000
C	1.587427000	1.042523000	0.075794000
H	0.679284000	1.625844000	0.200853000
H	2.234723000	1.204808000	0.932153000
H	2.083171000	1.350878000	-0.839569000
S	1.055761000	-0.690885000	-0.021236000

43.32 cm^{-1}

Figure 12 from main-text

a)

N	-2.479210000	-0.154947000	-0.000007000
H	-1.460290000	-0.042897000	0.000305000
H	-2.825333000	0.808874000	0.000719000

C	2.035205000	-0.047166000	0.000260000
H	3.091228000	-0.199043000	0.000679000
N	0.905376000	0.114384000	-0.000459000

26.30 cm^{-1}

b)

N	2.611662000	-0.141921000	-0.002299000
H	1.591110000	-0.042083000	0.011579000
H	2.946211000	0.826094000	-0.011208000
C	-0.898822000	0.078661000	0.010411000
N	-2.053981000	-0.021318000	-0.004267000
H	-3.048150000	-0.113303000	-0.016871000

63.85 cm^{-1}

c)

N	-1.792966000	0.126082000	0.000666000
H	-0.791631000	-0.106944000	-0.007112000
H	-2.259242000	-0.785684000	-0.003718000
N	1.452955000	-0.032605000	-0.001140000
H	1.536694000	0.964980000	-0.154656000
H	2.000125000	-0.491668000	-0.718414000
H	1.894129000	-0.235017000	0.887214000

144.15 cm^{-1}

d)

N	-2.710702000	0.132871000	-0.004387000
H	-1.708353000	-0.088015000	0.058124000
H	-3.153660000	-0.815944000	-0.007819000
P	1.201938000	-0.031368000	0.001789000
H	2.106872000	-0.634134000	-0.903188000
H	2.049944000	-0.204195000	1.121833000
H	1.651047000	1.282711000	-0.265073000

13.58 cm^{-1}

e)

N	2.204836000	-0.263269000	-0.005136000
H	2.959831000	0.512933000	0.040015000
H	1.259256000	0.252349000	-0.003057000
C	-1.372193000	-0.537242000	0.002710000
H	-0.623566000	-1.334190000	0.001711000
H	-1.991032000	-0.650785000	0.902484000
H	-2.011340000	-0.664554000	-0.879362000
O	-0.682969000	0.692425000	-0.007677000
H	-1.330094000	1.411179000	0.019322000

98.65 cm^{-1}

Figure 13 from main-text

a)

N	1.295590000	-0.000109000	-0.000207000
H	1.909435000	-0.815947000	0.000759000
H	1.907504000	0.817180000	0.000757000
F	-1.382975000	-0.000001000	0.000122000
H	-0.439290000	-0.000453000	-0.001163000

208.42 cm^{-1}

b)

N	-2.042992000	-0.000010000	-0.000127000
H	-2.662492000	-0.813316000	0.000263000
H	-2.662074000	0.813613000	0.000263000
H	-0.141965000	-0.000436000	0.000646000
Cl	1.162793000	0.000012000	-0.000017000

125.41 cm^{-1}

c)

N	-1.476664000	-0.032661000	0.015413000
H	-2.242332000	-0.676979000	-0.195096000
H	-1.930134000	0.872679000	0.160467000
H	1.910978000	-0.680179000	0.337844000
H	0.552053000	-0.057461000	-0.005233000
O	1.505761000	0.096321000	-0.050734000

64.15 cm^{-1}

d)

N	-2.335016000	0.009916000	-0.053114000
H	-2.962570000	0.786795000	0.172057000
H	-2.865551000	-0.823497000	0.215185000
S	1.297502000	-0.080322000	0.008977000
H	1.440372000	1.250219000	0.046000000
H	-0.027173000	0.002224000	-0.205078000

80.99 cm^{-1}

e)

N	-2.218539000	-0.000030000	0.000068000
H	-2.844951000	0.808870000	0.000246000
H	-2.845950000	-0.808158000	0.000248000
C	1.021122000	-0.000148000	-0.000267000
H	-0.055386000	-0.000364000	-0.000298000

N	2.164189000	0.000108000	0.000133000

69.69 cm^{-1}

f)

N	-1.980738000	0.000073000	-0.000346000
H	-2.600433000	-0.812657000	0.000770000
H	-2.600455000	0.812786000	0.000772000
C	2.097904000	0.000288000	-0.000168000
N	0.937366000	-0.000343000	0.000207000
H	-0.082933000	0.000029000	0.000441000

111.20 cm^{-1}

g)

N	2.457528000	-0.115462000	0.000086000
H	2.207141000	-0.697092000	-0.804840000
H	2.211151000	-0.702317000	0.802466000
C	-0.302973000	0.827201000	0.000314000
H	0.433290000	1.606819000	0.000536000
P	-1.349096000	-0.290825000	-0.000043000

45.74 cm^{-1}

h)

N	2.081216000	0.115742000	0.000573000
H	2.464013000	1.063970000	-0.013846000
H	2.901632000	-0.494839000	0.012173000
C	-1.474639000	0.469786000	0.001467000
H	-2.539367000	0.243486000	-0.000088000
H	-1.253638000	1.066473000	0.892135000
H	-1.252331000	1.072543000	-0.884784000
O	-0.776241000	-0.753131000	-0.002206000
H	0.168935000	-0.555492000	-0.000755000

25.52 cm^{-1}

i)

N	-2.492986000	-0.157191000	-0.003606000
H	-2.818740000	0.813321000	-0.033332000
H	-3.357713000	-0.703338000	0.047761000
C	0.667503000	1.163080000	0.003473000
H	1.596556000	1.727199000	0.006954000
H	0.101420000	1.417876000	-0.887828000
H	0.097976000	1.412610000	0.894069000
H	-0.135054000	-1.056342000	-0.005547000
S	1.122590000	-0.593092000	-0.001105000

30.27 cm^{-1}

Figure 14 from main-text

a)

N	2.283091000	0.176417000	-0.029896000
H	2.479612000	-0.706145000	-0.511074000
H	2.272727000	-0.092947000	0.957976000
C	-0.885978000	1.134273000	-0.012758000
H	0.033546000	1.536669000	-0.428868000
H	-1.731410000	1.437631000	-0.622638000
H	-1.001671000	1.495505000	1.004709000
S	-0.679822000	-0.670270000	-0.041306000
H	-1.841415000	-0.986946000	0.546615000

90.90 cm^{-1}

Figure 15 from main text

a)

H	-0.937053000	0.614786000	0.000057000
O	0.852279000	0.700358000	-0.000001000
O	1.038635000	-0.588971000	-0.000006000
H	0.139289000	-0.983526000	0.000060000
F	-1.592173000	-0.058040000	-0.000007000

217.67 cm^{-1}

b)

H	-0.485969000	0.798115000	0.000479000
O	1.512915000	0.686561000	-0.000012000
O	1.617101000	-0.611507000	0.000080000
H	0.697764000	-0.956538000	0.000077000
Cl	-1.485407000	-0.026001000	-0.000065000

151.79 cm^{-1}

c)

O	1.614726000	-0.021186000	-0.089187000
H	1.155563000	0.826398000	-0.036067000
H	2.289257000	-0.010976000	0.592849000
O	-1.069421000	0.661546000	0.011643000
O	-0.975503000	-0.640823000	0.008175000
H	-0.003231000	-0.811717000	-0.001827000

186.32 cm^{-1}

d)

S	1.545246000	-0.016260000	-0.086449000
H	1.814346000	-0.116991000	1.222032000
H	0.790451000	1.079578000	0.084436000
O	-1.722761000	0.657720000	0.007271000
O	-1.612811000	-0.643135000	0.004442000
H	-0.644160000	-0.819103000	-0.016990000

40.68 cm^{-1}

e)

C	-2.371153000	0.181915000	0.000066000
H	-3.354158000	0.597761000	0.000204000
N	-1.321044000	-0.259958000	-0.000075000
O	1.764048000	0.692227000	0.000037000
O	1.521611000	-0.593131000	-0.000035000
H	0.543104000	-0.662310000	-0.000092000

53.18 cm^{-1}

f)

H	-3.290783000	0.514730000	-0.000032000
O	1.760239000	0.705208000	0.000020000
O	1.607085000	-0.592948000	-0.000055000
H	0.629382000	-0.722117000	0.000045000
N	-2.365104000	0.138836000	-0.000085000
C	-1.286910000	-0.277090000	0.000144000

53.18 cm^{-1}

g)

C	-2.573522000	0.224895000	0.000066000
H	-3.592335000	0.555788000	0.000069000
P	-1.110817000	-0.213550000	0.000070000
O	1.988620000	0.776661000	-0.000109000
O	2.293178000	-0.493109000	-0.000080000
H	1.441342000	-0.970335000	0.000002000

46.27 cm^{-1}

h)

C	1.360745000	0.977074000	-0.000170000
H	1.441244000	2.046563000	-0.000184000
P	1.304093000	-0.554130000	0.000069000
O	-1.750204000	-0.681833000	-0.000157000
O	-1.789971000	0.619569000	0.000090000
H	-0.845703000	0.901061000	0.000714000

79.52 cm^{-1}

i)

N	-1.662194000	0.040481000	0.000002000
H	-1.386099000	1.016588000	-0.000099000
H	-2.235365000	-0.120928000	0.818207000
H	-2.235406000	-0.121077000	-0.818142000
O	1.274199000	0.602205000	0.000000000
O	0.922882000	-0.657142000	0.000001000
H	-0.084420000	-0.618451000	0.000015000

96.48 cm^{-1}

j)

H	1.857684000	1.012259000	-0.881838000
H	2.764079000	-0.545403000	0.200532000
H	1.381807000	0.703057000	1.192403000
O	-1.618220000	0.696817000	0.004498000
O	-1.724271000	-0.605002000	-0.000928000
H	-0.794241000	-0.925934000	-0.114930000
P	1.435373000	-0.065233000	-0.028315000

106.91 cm^{-1}

k)

O	-0.896116000	-0.042139000	-0.494258000
H	-0.465566000	-0.894499000	-0.361834000
C	-2.089780000	0.023852000	0.273313000
H	-2.519562000	1.008659000	0.110883000
H	-2.806480000	-0.729676000	-0.054820000
H	-1.889628000	-0.104489000	1.338286000
O	1.755872000	-0.636662000	0.132091000
O	1.589412000	0.656365000	0.048451000
H	0.626579000	0.756380000	-0.162669000

37.13 cm^{-1}

l)

S	-1.191683000	-0.673745000	0.063165000
H	-0.677661000	-0.639385000	1.300906000
C	-1.291635000	1.126059000	-0.179612000
H	-1.626553000	1.277421000	-1.202065000
H	-2.015898000	1.559866000	0.502306000
H	-0.314753000	1.580057000	-0.043106000
O	1.919903000	0.420979000	0.547227000
O	1.890958000	-0.308638000	-0.535789000
H	0.964710000	-0.653118000	-0.582514000

71.95 cm^{-1}

Figure 16 from main text

a)

F	-1.929249000	-0.136112000	0.000058000
H	-1.047752000	0.166031000	-0.000431000
O	0.680496000	0.644347000	-0.000008000
O	1.335963000	-0.482114000	-0.000090000
H	2.279322000	-0.238885000	0.000686000

90.79 cm^{-1}

b)

Cl	-1.729920000	-0.058429000	0.000008000
H	-0.515731000	0.373259000	0.000064000
O	1.494042000	0.693453000	-0.000015000
O	1.888742000	-0.550802000	-0.000090000
H	2.862091000	-0.521164000	0.000632000

75.16 cm^{-1}

c)

O	2.006204000	-0.207353000	-0.000683000
H	2.636399000	0.514831000	0.003315000
H	1.137887000	0.209693000	0.000817000
O	-0.869462000	0.698869000	-0.000206000
O	-1.321962000	-0.525769000	0.000861000
H	-2.292527000	-0.450496000	-0.003907000

72.72 cm^{-1}

d)

S	1.648430000	-0.098455000	0.000014000
H	2.552226000	0.888222000	0.000014000
H	0.614528000	0.754701000	0.000087000
O	-1.791180000	0.704021000	0.000019000
O	-1.592065000	-0.588019000	-0.000196000
H	-2.475677000	-0.995656000	0.001089000

48.91 cm^{-1}

e)

C	0.871906000	1.382029000	0.000000000
H	0.000000000	0.758377000	0.000000000
N	1.802160000	2.045719000	0.000000000
O	-1.486597000	-0.815554000	0.000000000
O	-0.604955000	-1.779580000	0.000000000
H	-1.114148000	-2.609511000	0.000000000

61.09 cm^{-1}

f)

N	0.734311000	1.375814000	0.000000000
H	0.000000000	0.682127000	0.000000000
C	1.581597000	2.169270000	0.000000000
O	-1.257241000	-0.785359000	0.000000000
O	-0.445067000	-1.805886000	0.000000000
H	-1.011295000	-2.598488000	0.000000000

56.98 cm^{-1}

g)

C	-0.991269000	0.208186000	0.000000000
H	0.000000000	0.622007000	0.000000000
P	-2.400979000	-0.386723000	0.000000000
O	2.318272000	0.925001000	0.000000000
O	2.494773000	-0.370207000	0.000000000
H	3.457934000	-0.508621000	0.000000000

41.08 cm^{-1}

h)

O	-1.455672000	-0.688695000	-0.344716000
H	-0.535407000	-0.916766000	-0.184869000
C	-1.691918000	0.583274000	0.218609000
H	-2.752637000	0.797716000	0.104184000
H	-1.448863000	0.609952000	1.284850000
H	-1.124339000	1.367642000	-0.290360000
O	1.442745000	-0.546373000	0.432523000
O	1.690599000	0.469803000	-0.350107000
H	2.591378000	0.763930000	-0.127061000

10.62 cm^{-1}

i)

S	-1.250882000	-0.690049000	0.000022000
H	-0.065023000	-0.067992000	0.000269000
C	-2.277880000	0.807757000	-0.000061000
H	-3.311635000	0.472248000	-0.000239000
H	-2.100214000	1.402096000	0.891307000
H	-2.099936000	1.402216000	-0.891293000
O	2.168583000	0.837014000	0.000075000
O	2.548510000	-0.414068000	-0.000001000
H	3.521455000	-0.397887000	-0.000621000

43.42 cm^{-1}

Figure 17 from main text

a)

F	2.077239000	-0.113137000	-0.000133000
H	1.151839000	-0.093261000	0.001015000
O	-1.671586000	-0.437241000	-0.000127000
O	-0.676085000	0.413102000	0.000287000
H	-1.065618000	1.304606000	-0.001099000

71.85 cm^{-1}

Co-ordinates of the Complexes with Positive Interaction Energy (UM06-2x/augg-cc-pVTZ)

S1)

O	-0.147378000	-3.184160000	0.000000000
H	0.488455000	-2.448868000	0.000000000
H	0.143757000	3.330829000	0.000000000
C	0.091135000	2.260791000	0.000000000
P	0.000000000	0.735105000	0.000000000

14.99 cm^{-1}

S2)

O	3.131385000	-0.075850000	-0.000311000
H	3.516685000	0.824060000	0.000644000
C	-0.305531000	-0.097897000	0.000616000
H	0.765598000	-0.191894000	0.001256000
P	-1.833345000	0.037468000	-0.000207000

83.72 cm^{-1}

S3)

O	1.370401000	-0.090516000	-0.000001000
H	1.349137000	0.880506000	0.000115000
N	-1.328447000	-0.053845000	-0.000039000
H	-0.824815000	-0.368158000	-0.819352000
H	-0.825479000	-0.367693000	0.819848000
H	-1.362922000	0.956384000	-0.000330000

129.03 cm^{-1}

S4)

O	1.978698000	-0.101222000	-0.000721000
H	1.929971000	0.869471000	-0.013530000
P	-1.109258000	-0.030062000	0.011938000
H	-0.638935000	1.179828000	-0.560087000
H	-0.227355000	-0.841056000	-0.734584000
H	-0.254390000	0.052466000	1.134893000

123.96 cm^{-1}

S5)

S	0.000000000	0.000000000	-2.573259000
H	0.000000000	0.000000000	-1.230768000
H	0.000000000	0.000000000	3.563855000
Cl	0.000000000	0.000000000	2.284650000

33.85 cm^{-1}

S6)

S	0.009929000	3.043415000	0.000000000
H	0.000000000	1.700940000	0.000000000
C	0.072745000	-3.280913000	0.000000000
H	0.159718000	-4.348719000	0.000000000
P	-0.050336000	-1.757425000	0.000000000

12.77 cm^{-1}

S7)

S	1.967946000	0.054418000	-0.000012000
H	3.108464000	-0.653972000	0.000114000
S	-2.020319000	-0.043110000	-0.000009000
H	-0.843402000	-0.683732000	0.000094000
H	-1.427092000	1.156774000	0.000123000

49.55 cm^{-1}

S8)

S	-1.103743000	-0.069616000	-0.001406000
H	-0.876197000	1.307296000	-0.020354000
N	1.750924000	0.008553000	-0.007477000
H	2.360600000	0.726960000	-0.416711000
H	1.939313000	-0.885570000	-0.476558000
H	1.979706000	-0.094696000	0.988457000

138.91 cm^{-1}

S9)

S	1.781441000	-0.078320000	0.000145000
H	1.595757000	1.319017000	-0.000206000
P	-1.798683000	-0.001896000	-0.000562000
H	-1.044348000	0.102184000	1.203542000
H	-1.018616000	0.964415000	-0.698272000
H	-1.055607000	-1.104066000	-0.498954000

97.41 cm^{-1}

S10)

S	1.625982000	-0.076730000	0.006060000
H	1.621057000	1.321218000	-0.136628000
S	-1.556595000	0.079215000	-0.054245000
H	-1.394845000	-0.145234000	1.270517000
H	-1.336407000	-1.215741000	-0.362930000

100.79 cm^{-1}

S11)

C	-0.891740000	0.039669000	0.001558000
H	0.180942000	0.076966000	0.002052000
P	-2.420773000	-0.017465000	-0.000402000
N	2.660622000	0.029088000	-0.001717000
C	3.809455000	-0.042771000	0.001108000

57.61 cm^{-1}

S12)

N	1.796543000	0.043565000	0.000042000
C	2.945832000	-0.038571000	0.000018000
Cl	-1.609531000	-0.003611000	-0.000093000
H	-2.888772000	-0.012138000	0.001177000

37. 56 cm^{-1}

S13)

N	1.110836000	0.439504000	0.020208000
C	1.980781000	-0.357809000	-0.020665000
S	-1.081965000	-0.148395000	-0.032561000
H	-1.237363000	1.018340000	-0.673100000
H	-1.111739000	0.426308000	1.176612000

121.21 cm^{-1}

S14)

C	-1.398119000	0.445370000	0.000005000
N	-0.720696000	-0.526378000	0.000001000
N	1.286485000	0.089339000	0.000003000
H	1.272669000	1.096833000	-0.000353000
H	1.577758000	-0.355171000	-0.854897000
H	1.577770000	-0.354611000	0.855188000

30.02 cm^{-1}

S15)

C	-0.858519000	-0.493276000	0.000064000
N	-1.679812000	0.314992000	-0.000029000
F	1.704773000	-0.015736000	-0.000035000

H	1.566840000	0.896337000	0.000137000

74.10 cm^{-1}

S16)

N	0.186426000	-2.335107000	0.000000000
C	-0.418849000	-1.353971000	0.000000000
Cl	0.000000000	1.383300000	0.000000000
H	1.208109000	0.953482000	0.000000000

73.97 cm^{-1}

S17)

N	0.931427000	-1.765453000	0.000000000
O	0.257552000	-2.679949000	0.000000000
S	-0.574395000	1.910200000	0.000000000
H	0.000000000	0.700482000	0.000000000
H	0.609927000	2.534083000	0.000000000

20.19 cm^{-1}

S18)

N	1.691296000	0.588557000	0.011008000
O	2.144431000	-0.453587000	-0.013001000
P	-1.585196000	-0.044110000	-0.121413000
H	-1.406966000	1.198209000	0.526795000
H	-0.934904000	-0.775345000	0.899819000
H	-2.874714000	-0.252419000	0.421537000

53.35 cm^{-1}

S19)

O	0.000000000	0.954190000	0.000000000
N	-0.019434000	2.091401000	0.000000000
O	0.005842000	-2.343880000	0.000000000
H	-0.714757000	-1.710707000	0.000000000
H	0.804063000	-1.811581000	0.000000000

18.76 cm^{-1}

S20)

O	0.472730000	-1.983922000	0.000000000
N	0.673674000	-3.103098000	0.000000000
S	-0.569678000	2.121368000	0.000000000
H	0.000000000	0.910934000	0.000000000
H	0.617288000	2.740229000	0.000000000

36.49 cm^{-1}

S21)

O	1.241408000	0.002074000	0.114115000
N	2.359312000	-0.001816000	-0.093759000
N	-2.674339000	-0.000746000	-0.133956000
H	-1.668674000	-0.001568000	-0.021879000
H	-3.029701000	-0.812694000	0.354457000
H	-3.027703000	0.815604000	0.348508000

33.65 cm^{-1}

S22)

O	2.237594000	-0.000057000	0.086736000
N	3.363070000	0.000051000	-0.074338000
P	-2.344229000	0.000017000	-0.130166000
H	-0.970392000	-0.001655000	0.203149000
H	-2.655550000	-1.027972000	0.788273000
H	-2.652869000	1.029468000	0.787550000

37.54 cm^{-1}

S23)

O	-2.043525000	-0.621547000	0.130885000
N	-2.575009000	0.341974000	-0.155196000
H	0.596645000	-1.234247000	0.115248000
C	0.820718000	1.134723000	0.070896000
H	1.589209000	1.898220000	-0.017276000
H	0.105675000	1.260748000	-0.736646000
H	0.326797000	1.242641000	1.032387000
S	1.676914000	-0.462321000	-0.048737000

17.93 cm^{-1}

S24)

O	2.231033000	-0.042928000	0.000722000
N	1.098688000	0.066879000	-0.000805000
H	-3.378504000	0.060335000	0.007689000
F	-2.462287000	-0.020563000	-0.000870000

9.24 cm^{-1}

S25)

O	2.101745000	-0.482521000	-0.000016000
N	1.729956000	0.591527000	0.000054000
Cl	-1.540113000	0.008848000	-0.000052000
H	-2.741726000	-0.430947000	0.000638000

47.69 cm^{-1}

S26)

N	1.772027000	-0.561881000	0.024952000
O	2.288148000	0.449990000	-0.028501000
S	-1.645606000	-0.064569000	-0.003562000
H	-1.999406000	0.747533000	1.000538000
H	-2.380269000	0.618818000	-0.890203000

44.39 cm^{-1}

S27)

H	-0.269767000	3.577134000	0.000000000
N	-0.522339000	-1.781290000	0.000000000
O	0.595312000	-1.989458000	0.000000000
N	0.000000000	1.385181000	0.000000000
C	-0.139393000	2.518549000	0.000000000

16.75 cm^{-1}

S28)

N	2.489131000	0.085474000	-0.022482000
H	3.407095000	0.472582000	-0.085130000
C	1.420004000	-0.360961000	0.052029000
N	-1.646619000	0.593435000	0.020455000
O	-2.228088000	-0.382397000	-0.026607000

19.63 cm^{-1}

S29)

H	1.257439000	2.081264000	0.000048000
N	-2.056701000	-0.637992000	0.000053000
O	-2.215613000	0.486863000	-0.000046000
C	1.365395000	1.015410000	0.000032000
P	1.511467000	-0.506845000	-0.000016000

37.91 cm^{-1}

S30)

N	-1.778577000	0.553698000	0.006664000
O	-2.364330000	-0.420886000	-0.010788000
H	1.895745000	0.272309000	1.308590000
H	2.273284000	1.081896000	-0.549250000
H	2.777523000	-0.878781000	-0.158045000
P	1.627875000	-0.065615000	-0.037442000

45.03 cm^{-1}

S31)

H	-0.879139000	-2.616455000	0.000000000
F	-0.742259000	-1.706787000	0.000000000
O	0.000000000	1.364000000	0.000000000

N	1.079924000	1.009363000	0.000000000

50.62 cm^{-1}

S32)

O	-1.813376000	-0.524062000	0.000000000
N	-2.030447000	0.592033000	0.000000000
Cl	1.538111000	-0.039129000	0.000000000
H	2.572253000	0.713459000	0.000002000

38.01 cm^{-1}

S33)

H	-0.714811000	3.645510000	0.000000000
N	-0.379682000	-2.155557000	0.000000000
O	0.756784000	-2.141390000	0.000000000
N	-0.383097000	2.704139000	0.000000000
C	0.000000000	1.607589000	0.000000000

39.09 cm^{-1}

S34)

H	0.432736000	4.113598000	0.000000000
C	0.254905000	3.057178000	0.000000000
N	-0.160844000	-3.652162000	0.000000000
O	-0.104532000	-2.516517000	0.000000000
P	0.000000000	1.549373000	0.000000000

16.87 cm^{-1}

S35)

N	2.174709000	-0.615003000	0.004493000
O	2.255230000	0.519284000	-0.002211000
H	-1.844508000	1.330974000	-0.265677000
H	-2.687939000	-0.006794000	1.054004000
H	-2.690545000	-0.411595000	-0.966056000
P	-1.736120000	-0.050789000	0.010931000

14.22 cm^{-1}

S36)

N	2.549047000	-0.118979000	0.000054000
H	1.581342000	0.218112000	0.001784000
H	3.104883000	0.741368000	-0.001396000
H	-1.873672000	1.028882000	0.000583000
Cl	-1.215052000	-0.067971000	-0.000079000

59.69 cm^{-1}

S37)

N	-3.090980000	0.001521000	-0.000004000
H	-3.781200000	-0.754423000	0.000928000
H	-3.657791000	0.853834000	0.000546000
C	0.327140000	-0.036455000	-0.000601000
H	-0.749113000	-0.066419000	-0.000991000
P	1.857475000	0.011673000	0.000210000

88.94 cm^{-1}

S38)

N	-2.140340000	-0.013919000	-0.114641000
H	-2.089478000	-0.717408000	0.628135000
H	-2.079204000	0.873621000	0.393285000
H	2.111933000	0.151229000	0.569581000
Cl	1.002302000	-0.012354000	-0.046383000

92.02 cm^{-1}

S39)

N	2.112229000	-0.013752000	-0.000180000
H	2.031187000	0.615127000	0.804425000
H	2.032669000	0.618129000	-0.802618000
C	-1.088429000	0.916707000	0.000073000
H	-1.332905000	1.960067000	0.000122000
P	-0.732399000	-0.573153000	-0.000074000

48.28 cm^{-1}

S40)

N	1.959485000	0.000185000	0.130057000
H	2.078659000	-0.803057000	-0.494452000
H	2.075826000	0.802662000	-0.495957000
P	-0.917734000	0.000120000	-0.095783000
H	-0.885541000	-1.033337000	0.862871000
H	-2.329337000	-0.003062000	-0.209056000
H	-0.889990000	1.033695000	0.862938000

68.52 cm^{-1}

S41)

H	-1.248093000	0.613765000	0.022960000
H	-1.738433000	-0.908023000	0.310535000
H	-2.814447000	0.317113000	0.393696000
O	1.132644000	0.721258000	0.012344000
O	1.102673000	-0.585486000	0.030351000
H	2.025560000	-0.872505000	-0.212059000
N	-2.015303000	-0.033790000	-0.122384000

95.88 cm^{-1}

S42)

P	1.919947000	-0.066681000	-0.034848000
H	1.803724000	0.832280000	1.089314000
H	0.720720000	-0.771689000	0.325489000
H	1.199785000	0.792296000	-0.940798000
O	-1.971833000	-0.698835000	-0.003143000
O	-1.762514000	0.592301000	0.011145000
H	-2.648655000	0.999611000	-0.015294000

53.33 cm^{-1}

S43)

H	-3.024080000	-0.051629000	0.001582000
O	2.251927000	-0.587172000	0.001892000
O	1.558281000	0.521843000	-0.006678000
H	2.208876000	1.244006000	0.029838000
Cl	-1.745086000	-0.039396000	0.000404000

12.58 cm^{-1}

Table SI_41: W1U vs UCCSD(T)(FC)/aug-ccpVTZ// UM06-2x/aug-cc-pVTZ

From out of a total ~ 160 minimum energy structures obtained as part of this work, ~ 43 of them have a positive interaction energy, despite being fully optimized minimum energy structures. In case, there are systematic errors in the computed interaction energies, they could arise possibly due to the UCCSD(T)(FC)/aug-cc-pVTZ method's accuracy (~ 1 kcal/mol). To check it, we performed calculations on representative systems with the more accurate (~ 0.5 kcal/mol) W1U method. The resulting WIU energies are very similar to the energies obtained with the CCSD(T) method (within 1.5 kcal/mol).

S. No.	System	W1U[a] (kcal/mol)	UCCSD(T)/aug-cc-pVTZ//UM06-2x/aug-cc-pVTZ including BSSE corrections (kcal/mol)	UCCSD(T)/aug-cc-pVTZ//UM06-2x/aug-cc-pVTZ No BSSE corrections (kcal/mol)	Figure
1	SH···HCl	-0.07	1.42	1.34	S5
2	CN···HCl	-0.42	0.85	0.62	S12
3	CN···H_2S	2.21	2.86	1.89	S13
4	CN···NH_3	3.95	3.74	2.97	S14
5	CN···HF	-0.83	0.16	-0.17	S15
6	CN···HCl	-0.86	0.14	-0.31	S16
7	CN···H_2S	-0.78	0.57	0.31	S17
8	NO···H_2O	-0.56	0.00	-0.25	S19
9	SH···HCN	-2.44	-1.23	-1.58	3d (main text)
10	CN···H_2S	-10.48	-8.07	-8.95	8b (main text)

a. BSSE corrections were not carried out with the WIU method. Zero point corrections were included.

Attempts to optimize other isomers/electronic states alternative to the ones reported in the main-text

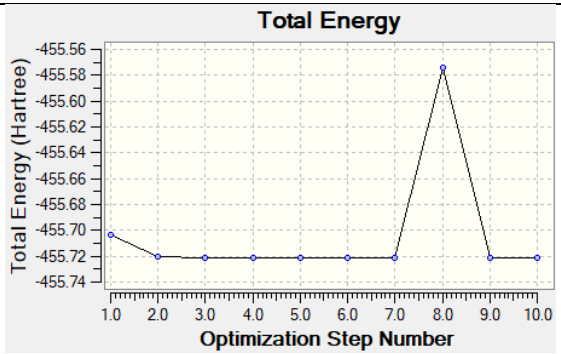
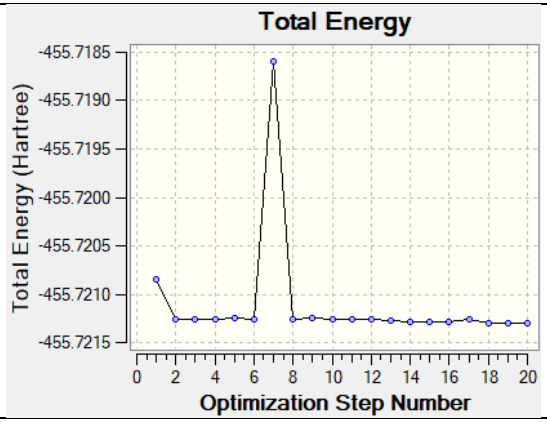
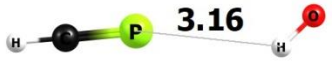
From out of a total ~ 160 structures obtained in this work, ~ 43 of them have a positive interaction energy, despite being fully optimized minimum energy structures. In case, there are systematic errors, they could also arise because, during the optimization of our structures, we might have missed out on more stable isomers/lower lying electronic states relative to the ones reported in the main text). Therefore, it becomes important to examine if there are other possible isomers.

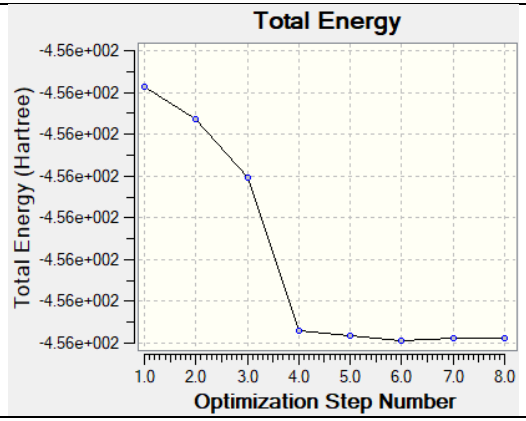
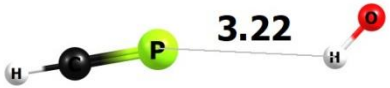
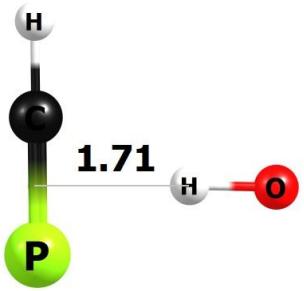
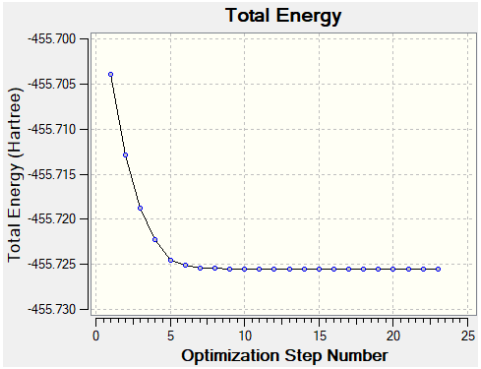
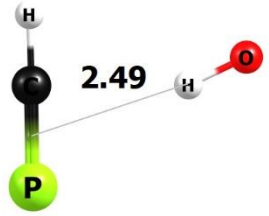
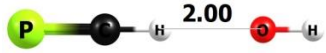
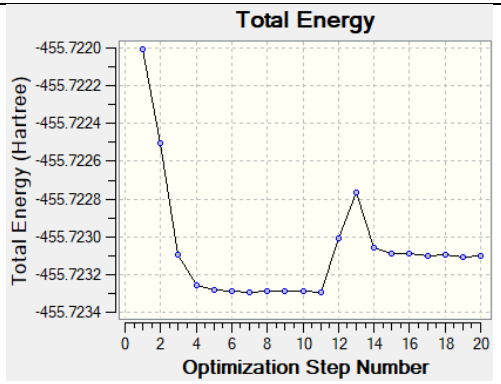
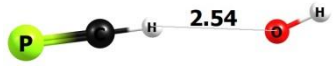
In the next 60-odd pages, we present our systematic and elaborate attempts to optimize alternate electronic states/isomers. What is shown is – (a) the geometry we attempt to optimize, (b) the optimization profile (if it is smooth or bumpy), (c) The geometry obtained at the end of each calculation (if it is a minimum energy structure or not), and (d) finally obtained minimum energy structure. It should be noted that we present this data for only the 43 structures having a positive interaction energy. Although we have done the same exercise for all the structures reported in the main-text (we shall gladly present that data also to interested readers upon request). What is also not shown is our attempt to optimize quartet, and sextet electronic states (which invariably end up having higher energy than the doublet states reported in the main-text).

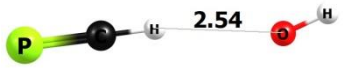
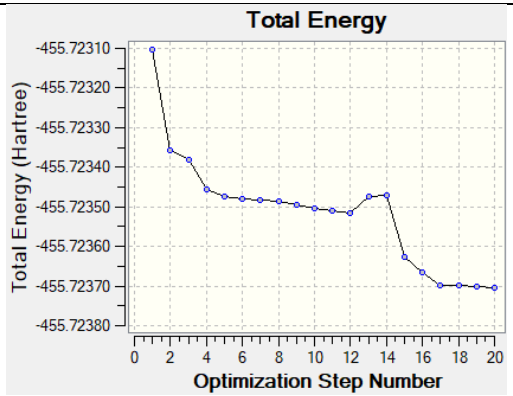
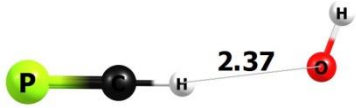
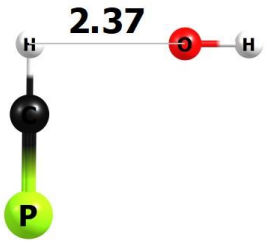
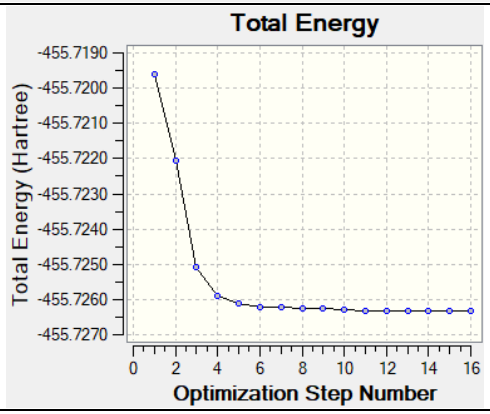
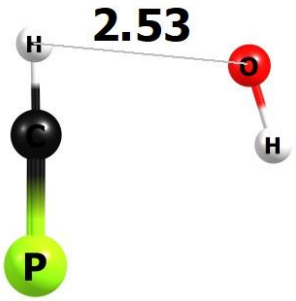
Our conclusion (*vide infra*) after doing this exercise is that, we ended up getting: (a) either the same optimized structures reported in this work, or (b) some other minimum energy structures not featuring weak interactions (full-fledged covalent bond getting formed) or (c) minimum energy structures wherein the interaction energies were again positive or (d) higher order saddle points containing at least one imaginary frequency.

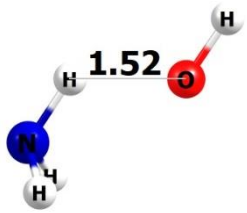
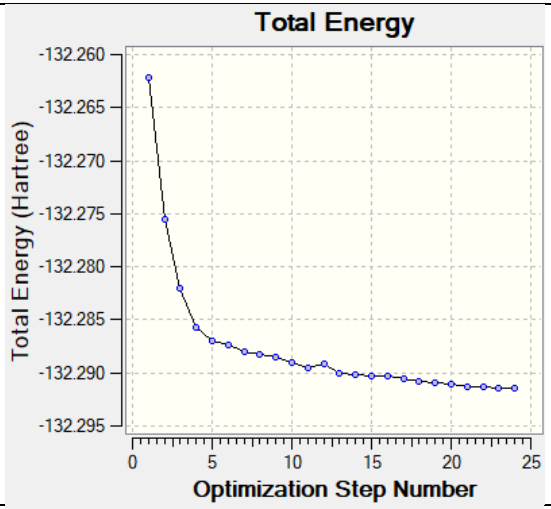
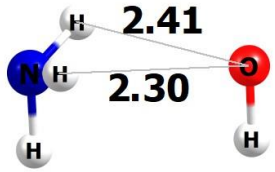
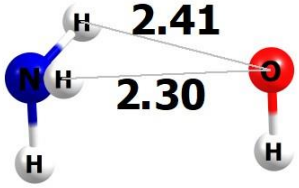
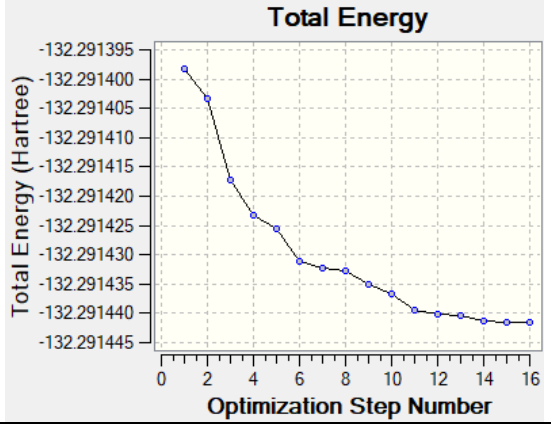
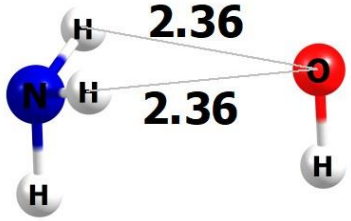
Another noteworthy point is that, a smooth optimization profile (following the Berny optimization algorithm using DIIS) typically implies that we don't miss any other minimum energy structure in-between the starting geometry and the minimized structure we get. A bumpy profile can sometimes indicate that there may be other minima which we need to consider. In case the profile was bumpy, we chose the point immediately preceding the bump, and again carried out optimization. By doing this exercise, we ended up with the same set of abovementioned conclusions (in the previous paragraph). So, we also do not include this data in the following pages (interested readers can avail this from us upon request). It should also be stated that even for the 43 structures in the main-text having a positive interaction energy, these are not the only attempts we made. For the sake of succinctness, we present only the most chemically intuitive starting geometries. What we do not show are several other starting geometries, which result in the same conclusions.

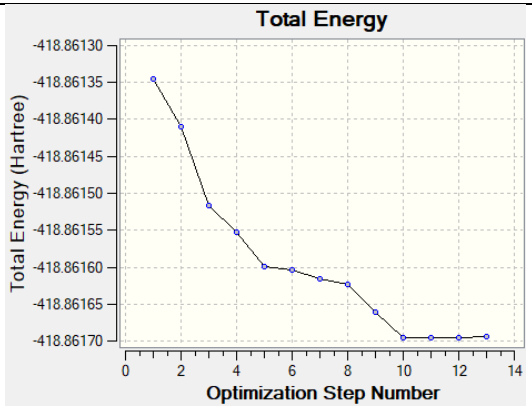
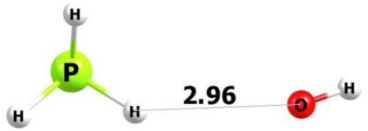
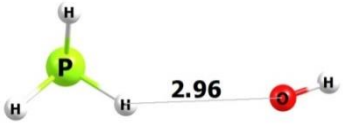
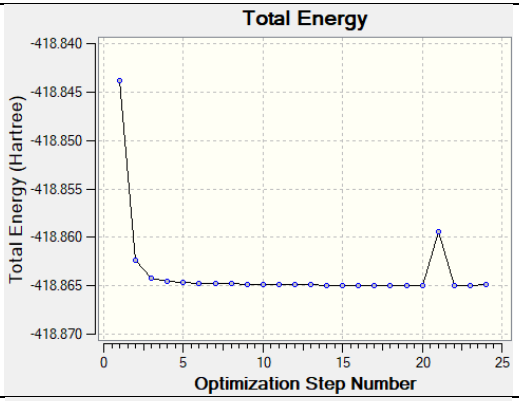
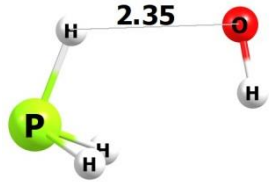
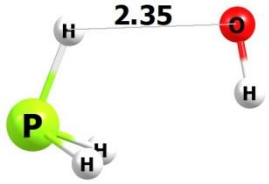
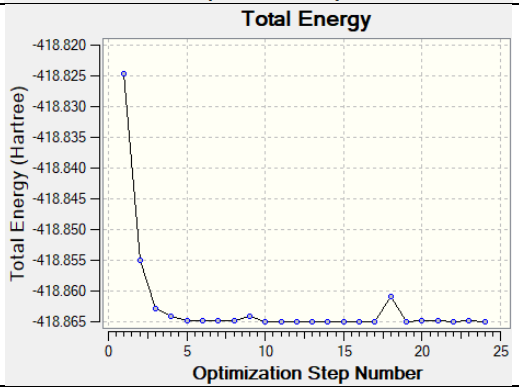
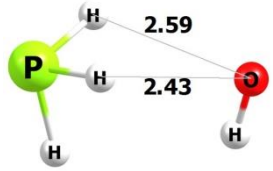
All the structures reported in the following pages have doublet electronic states, and are neutral. Level of theory used – UCCSD(T)(FC)/aug-cc-pVTZ//UM06-2x/aug-cc-pvTZ. They are all minimum energy structures with zero imaginary frequencies.

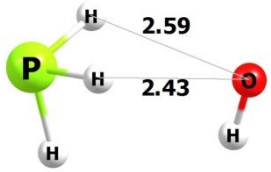
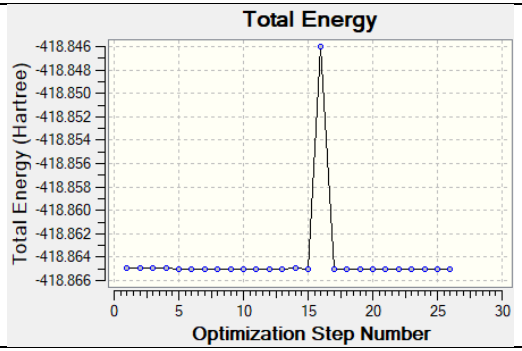
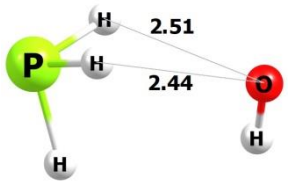
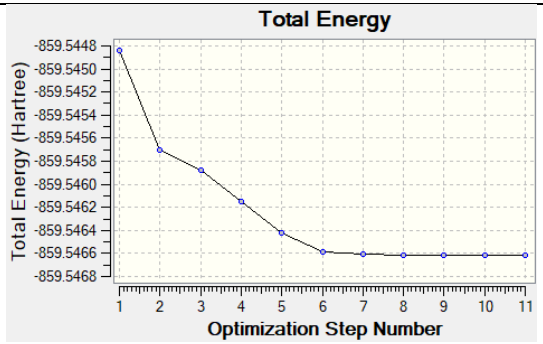
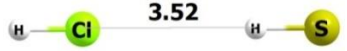
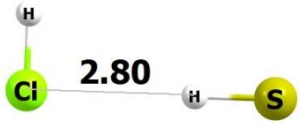
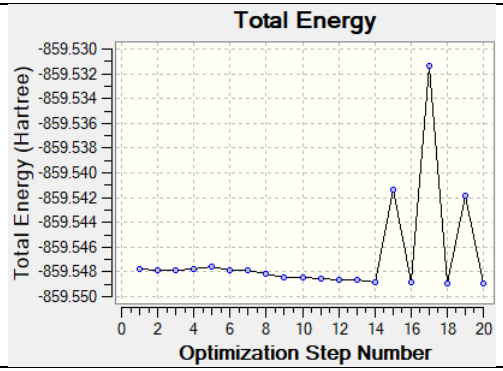
Systems	Isomer we attempted to optimize	Optimization Profile	Geometry obtained at the end of a calculation
OH···Molecules			
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S1	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

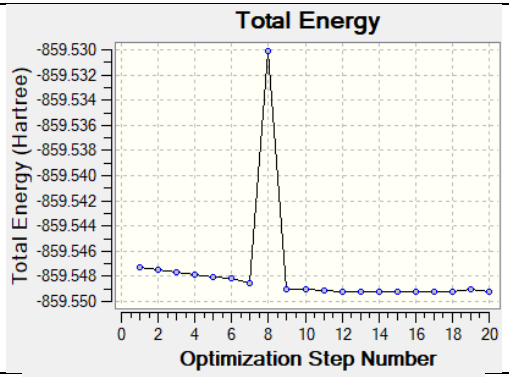
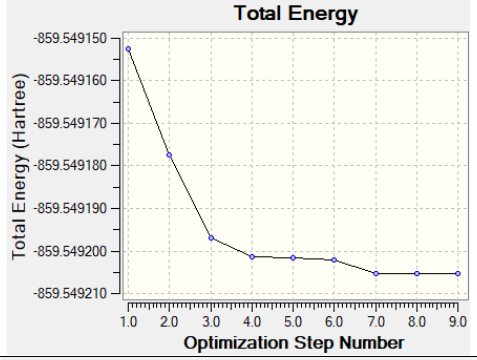
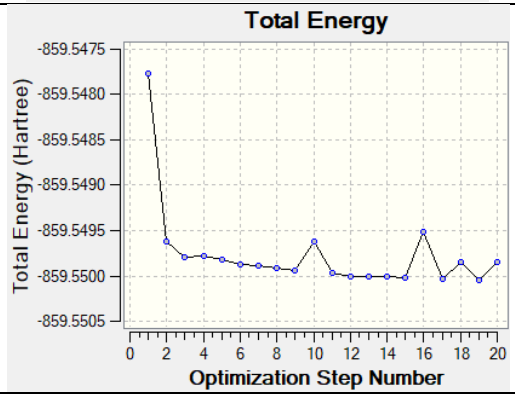
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S1 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. 1i ***New Isomer having lower interaction energy found***	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (1i in main text)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S2	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

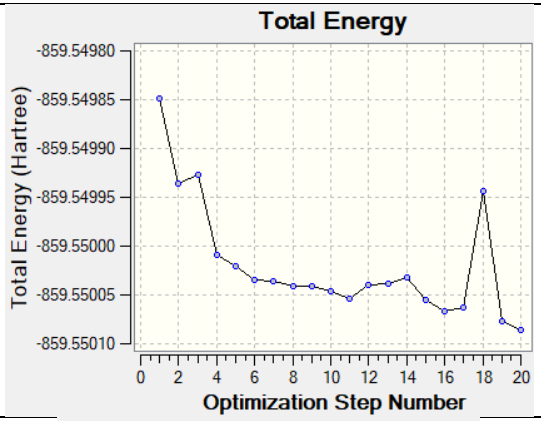
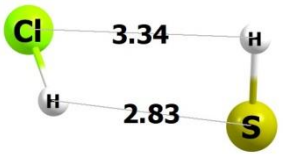
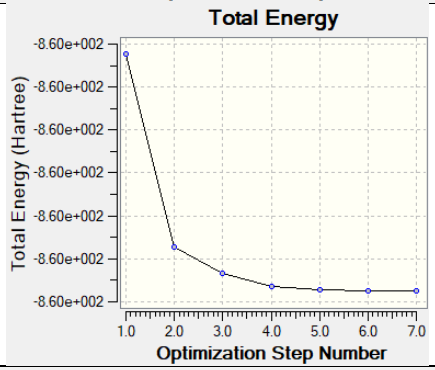
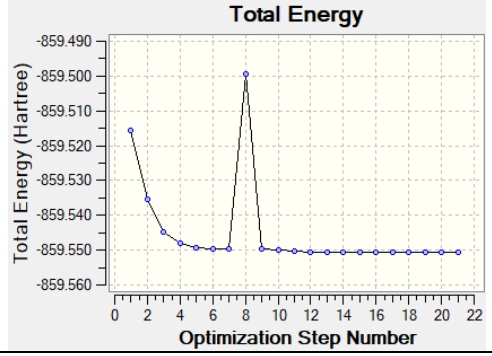
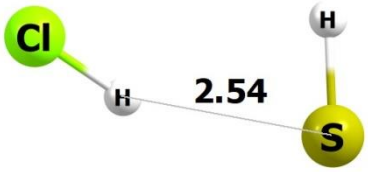
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S2 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. 2f ***New Isomer having lower interaction energy found***	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (2f in main text)**

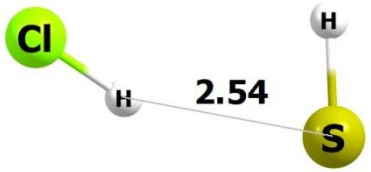
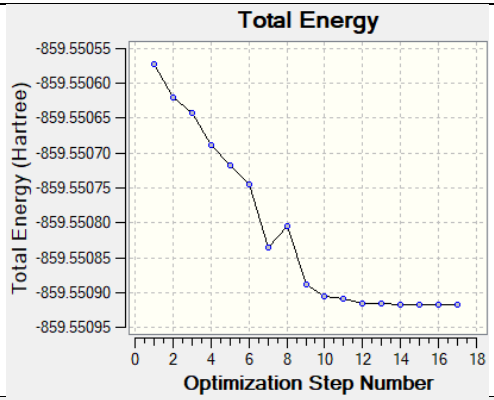
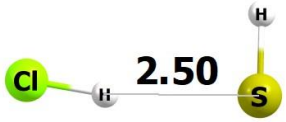
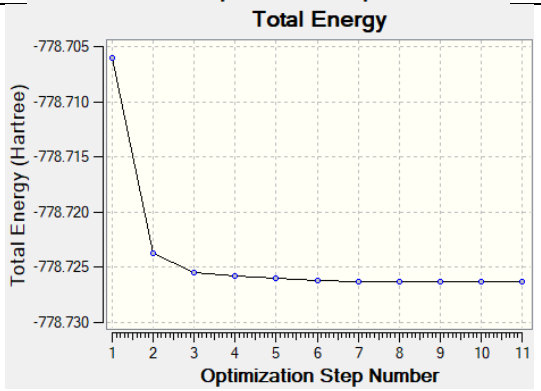
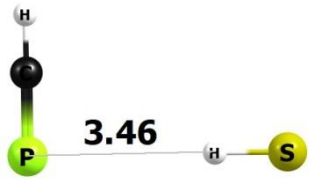
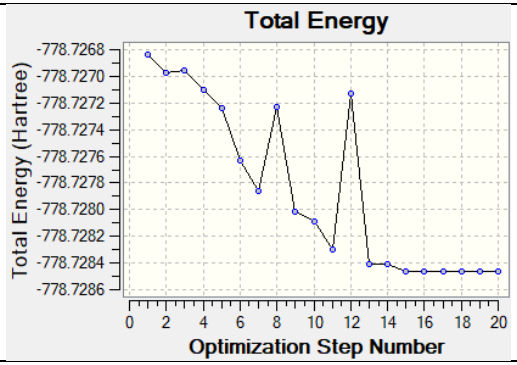
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S3	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S3 in the SI)**

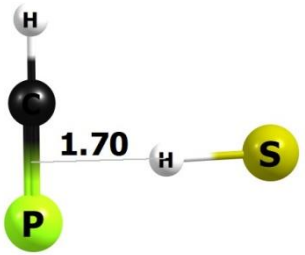
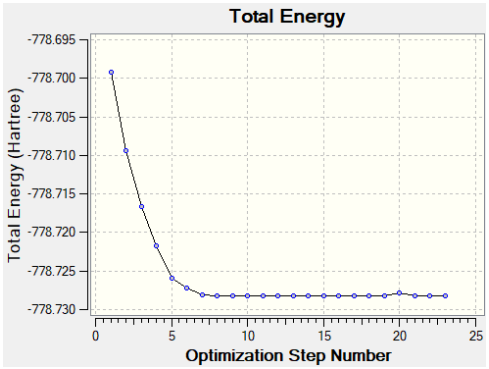
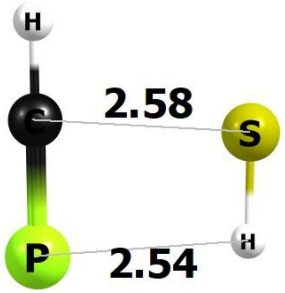
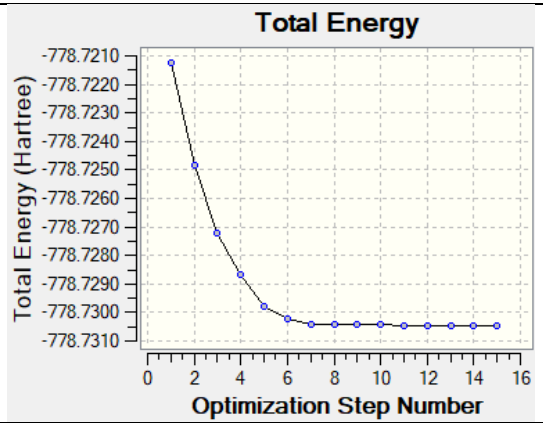
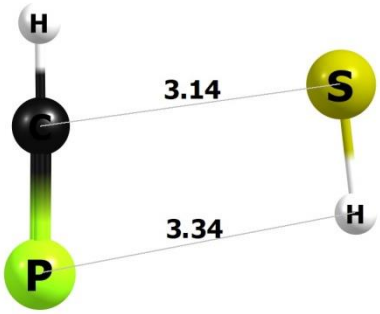
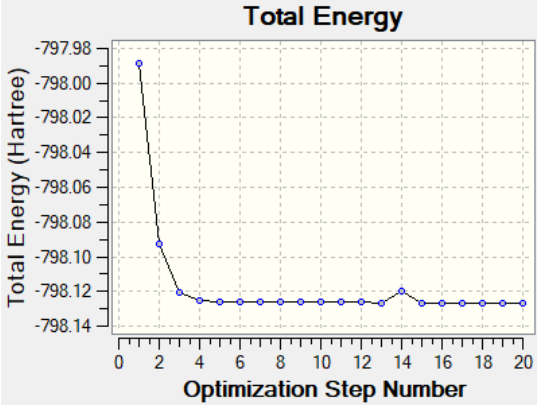
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S4	 **A** **Input structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**

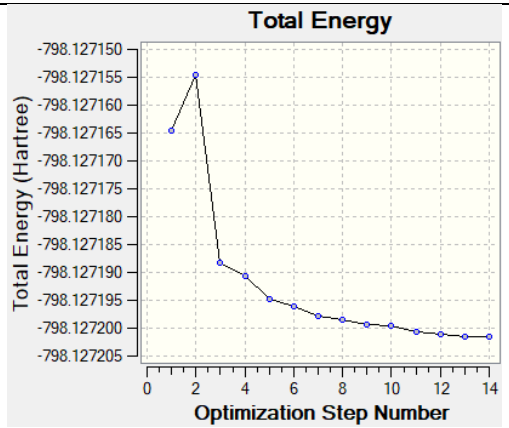
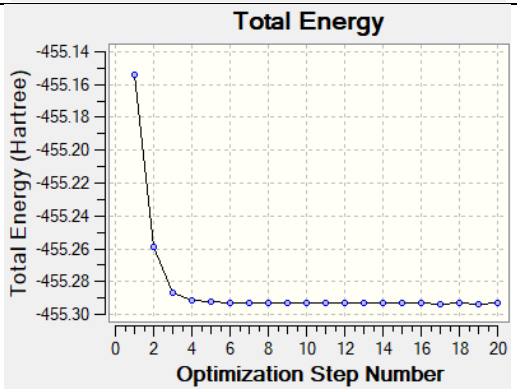
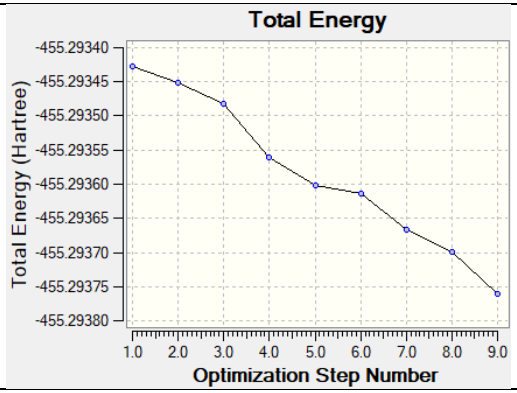
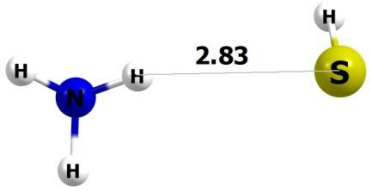
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E** (**S4 in the SI)**
SH···Molecules			
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S5	 **A** **Input structure**		 Fully optimized minimum energy structure **B** (**S5 in the SI)**
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S5	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

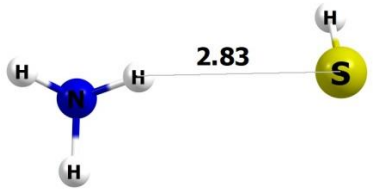
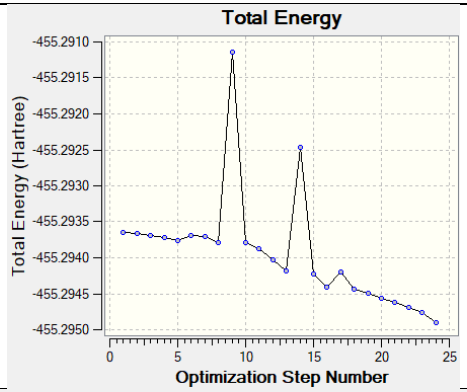
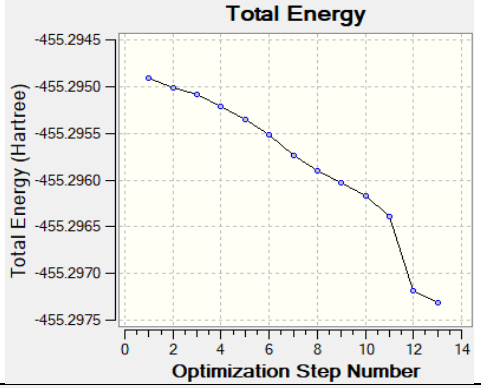
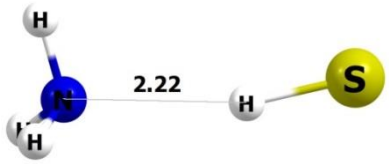
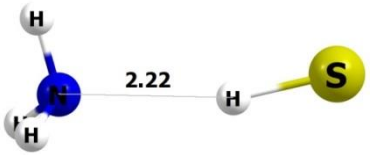
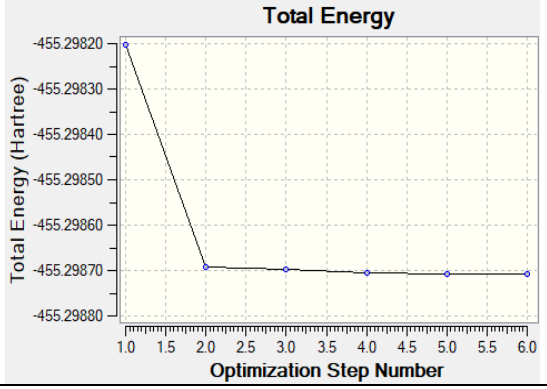
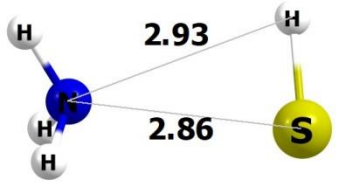
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**

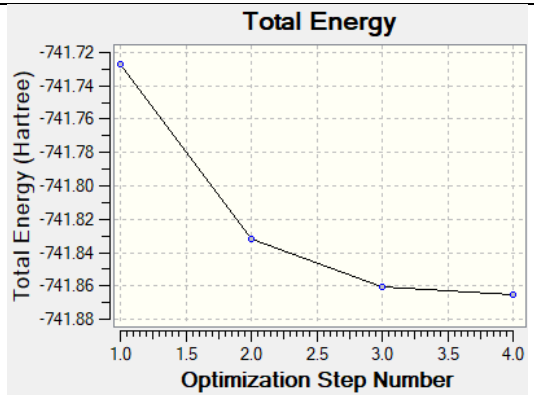
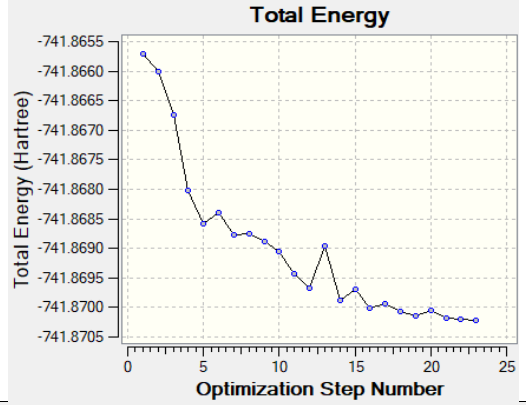
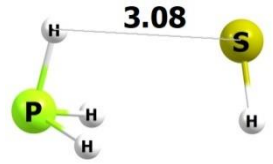
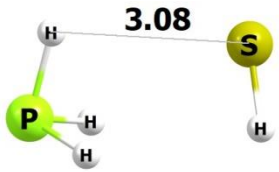
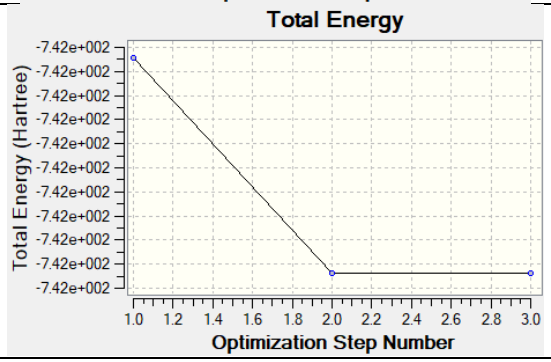
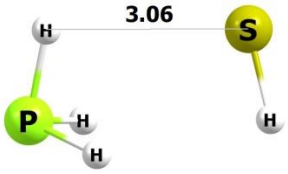
	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 (Job ended without giving any optimized minimum energy structure) **F**
	 (Starting an optimization calculation with the same non-optimized geometry **F**)		 (Job ended without giving any optimized minimum energy structure) **G**
	 (Starting an optimization calculation with the same non-optimized geometry **G**)		 (Job ended without giving any optimized minimum energy structure) **H**

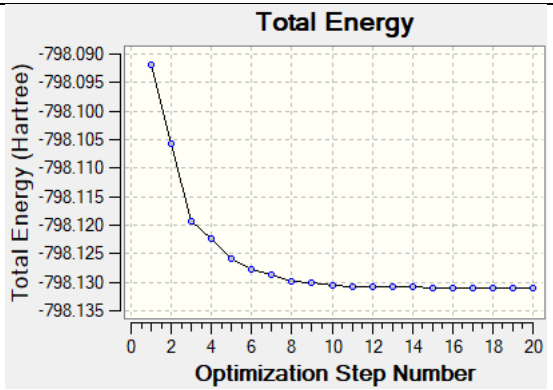
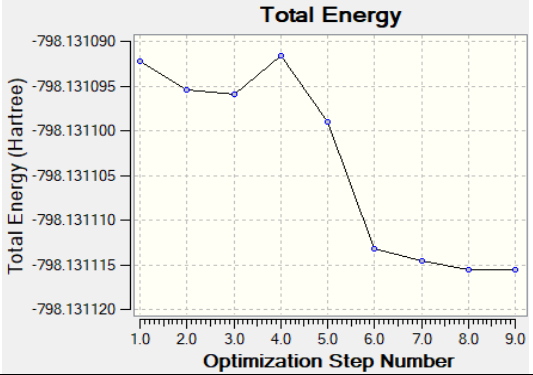
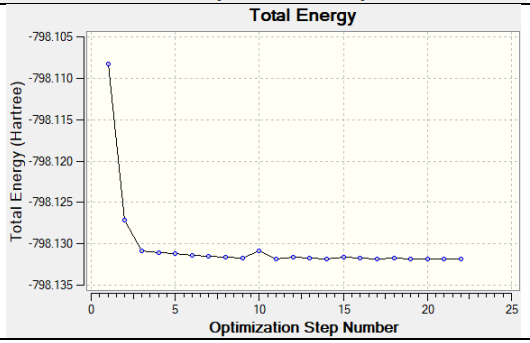
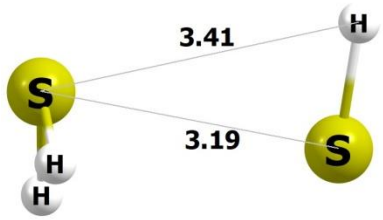
	 (Starting an optimization calculation with the same non-optimized geometry **H**)		 Fully optimized minimum energy structure **I (4b in the main text)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S6	 **A** **Input Structure**		 Fully optimized minimum energy structure **B** (**S6 in the SI**)
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S6	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (3f in the main text)**

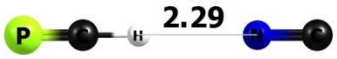
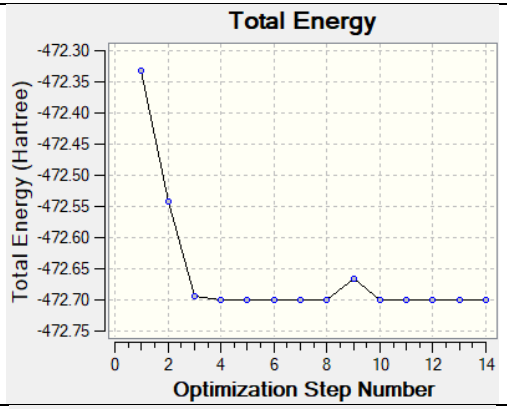
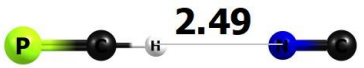
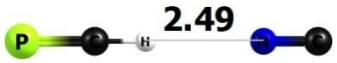
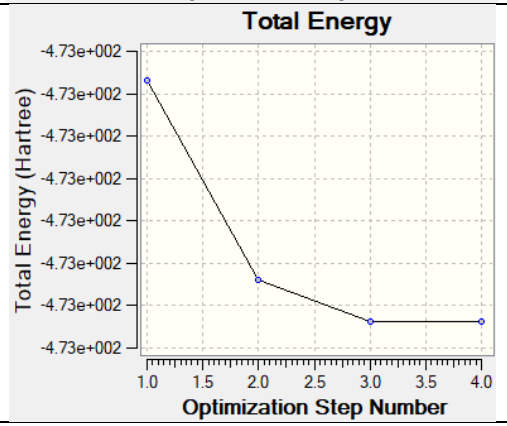
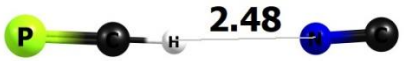
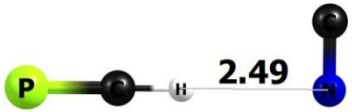
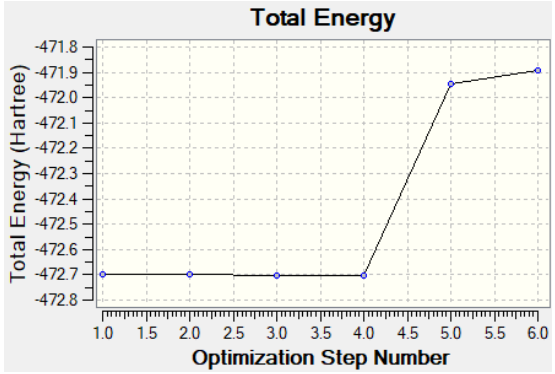
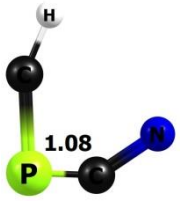
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. 3f ***New Isomer having lower interaction energy found***	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (3f in the main text)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. 3g ***New Isomer having lower interaction energy found***	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (3g in the main text)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S7	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

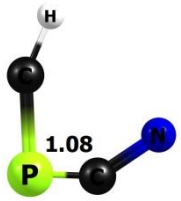
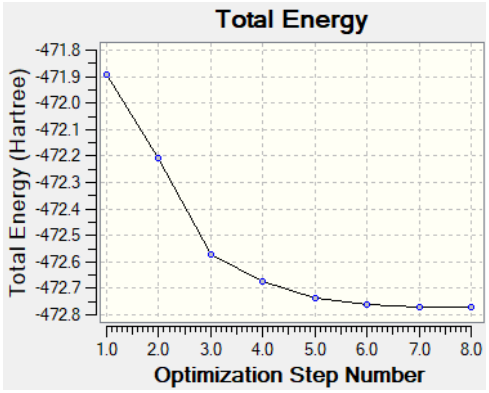
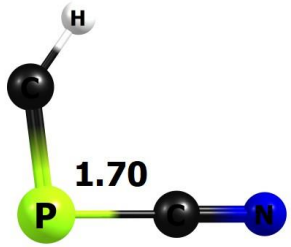
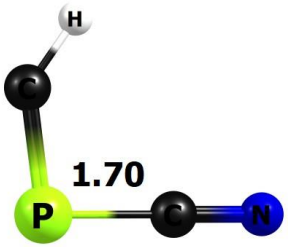
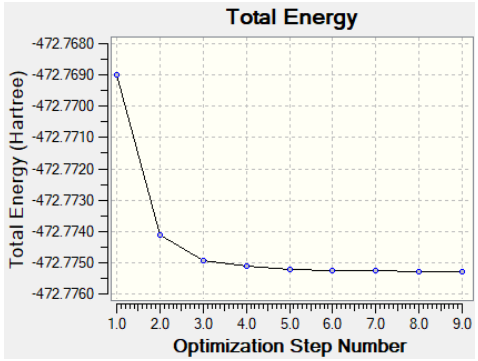
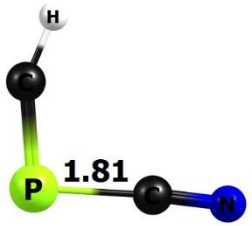
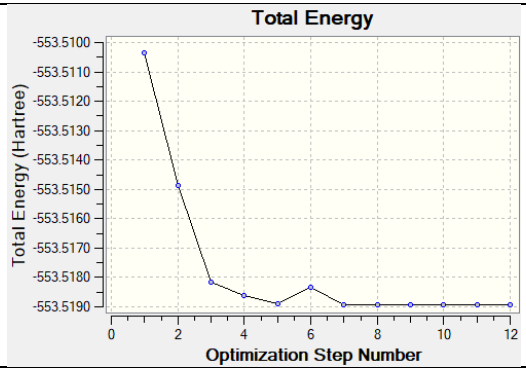
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S7 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S8	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

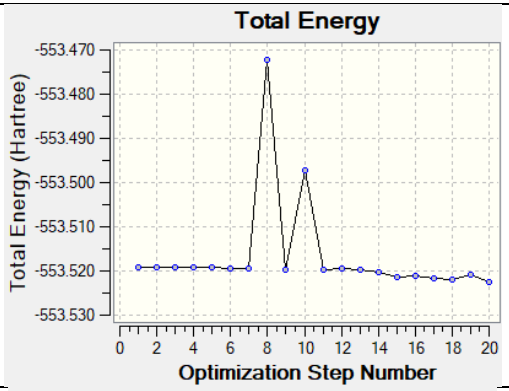
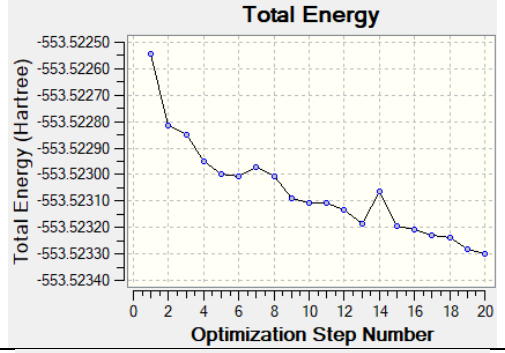
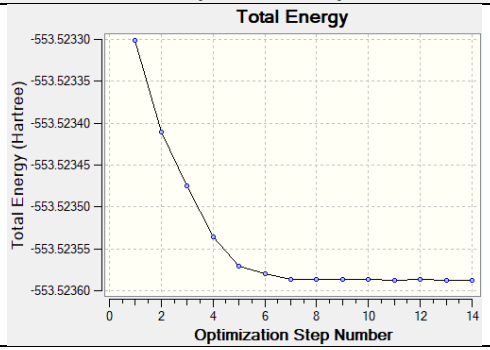
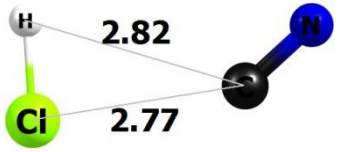
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**
	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 Fully optimized minimum energy structure **F** (**S8 in the SI)**

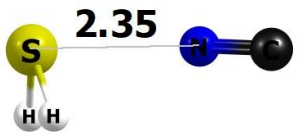
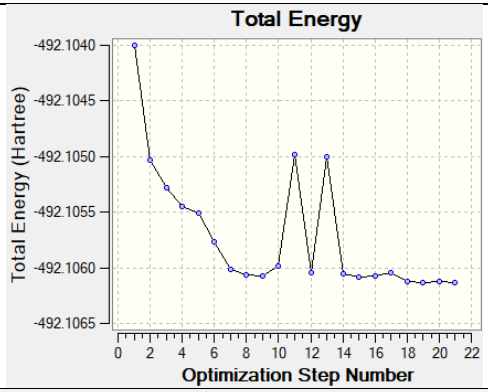
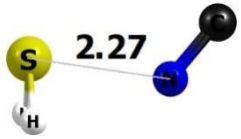
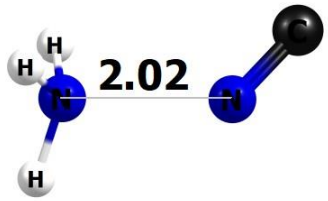
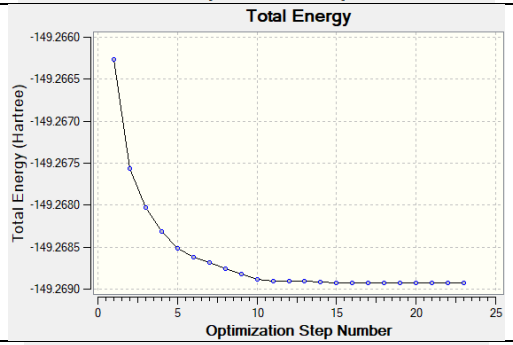
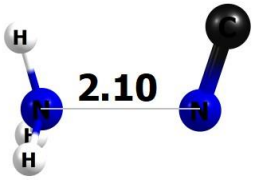
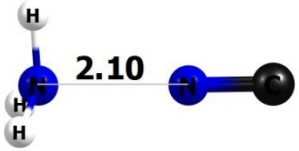
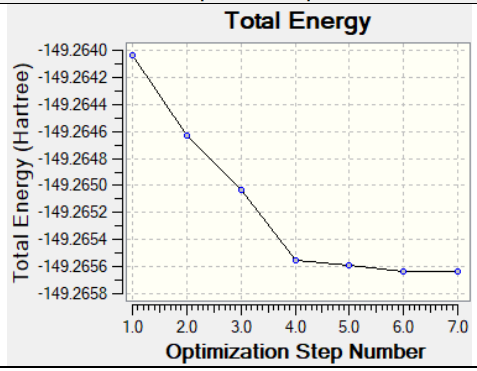
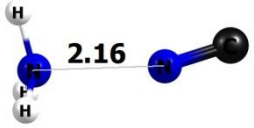
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S9	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S9 in the SI)**

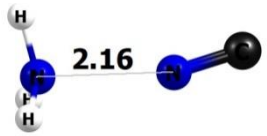
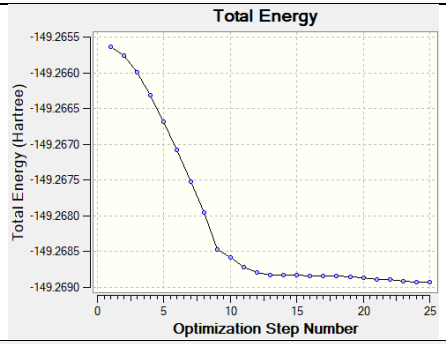
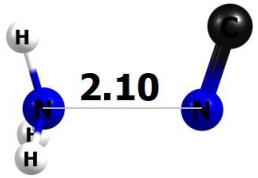
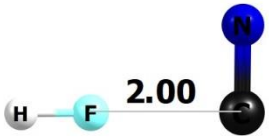
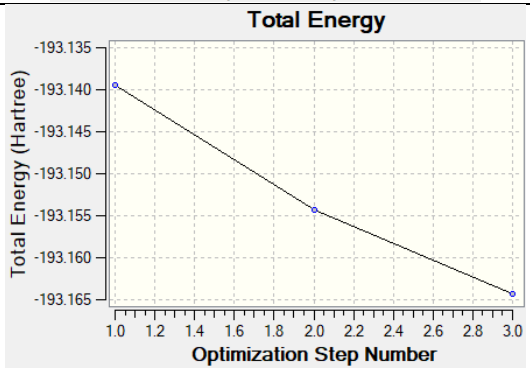
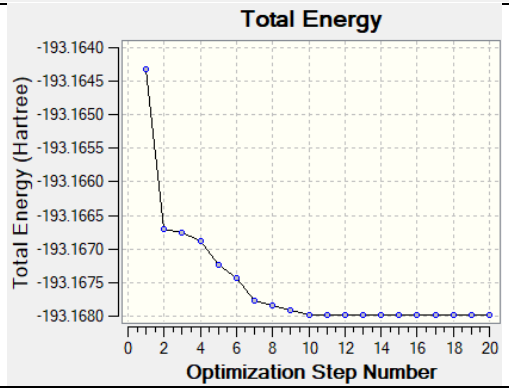
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S10	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S10 in the SI)**
CN···Molecules			

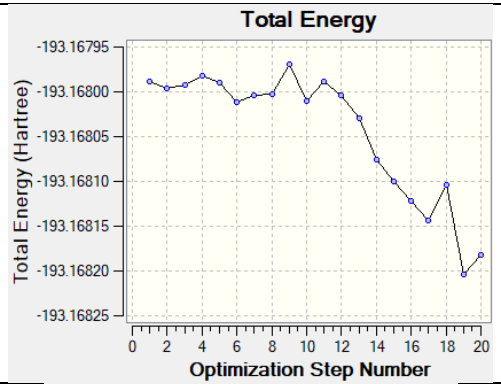
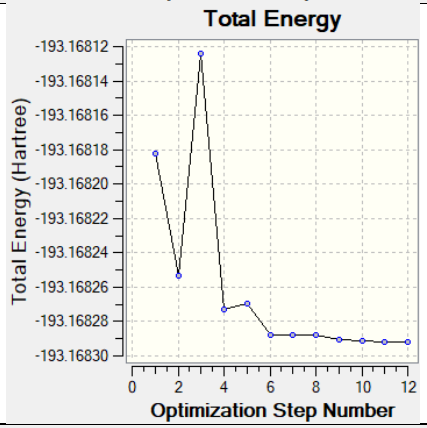
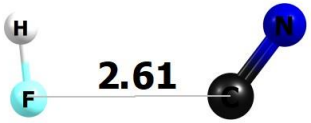
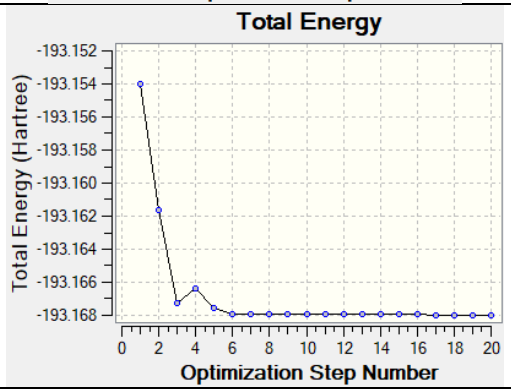
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S11	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C (S11 in the SI)**
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S11	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

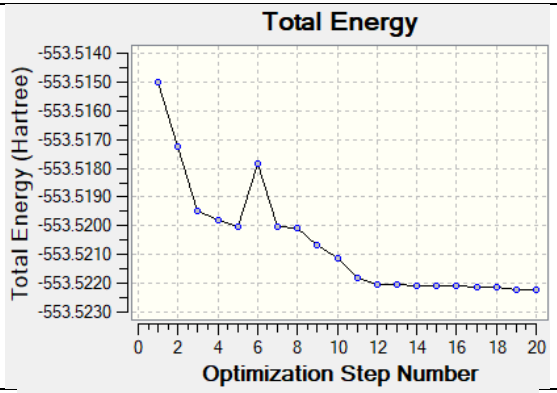
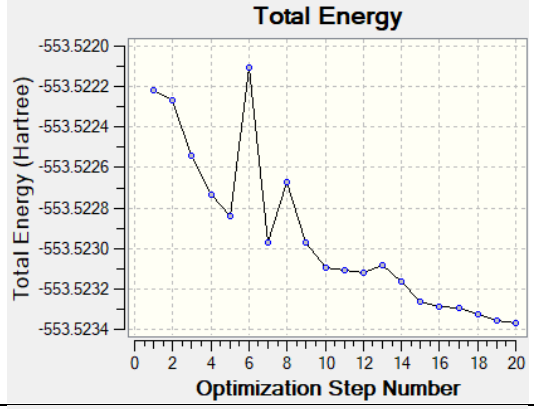
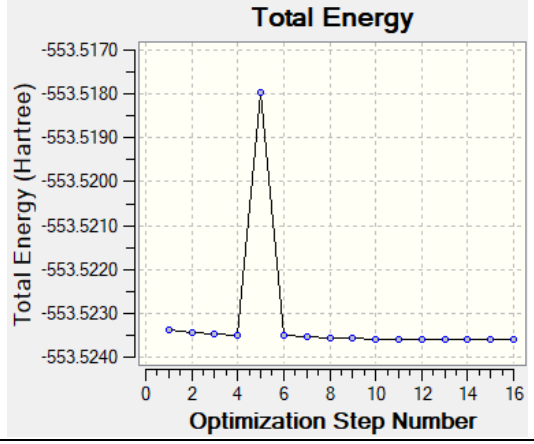
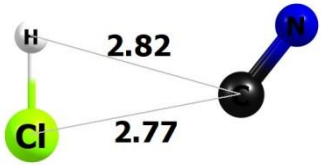
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D (not involving weak interaction, covalent bond between P and C formed)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S12	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (S12 in the SI)**

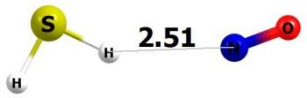
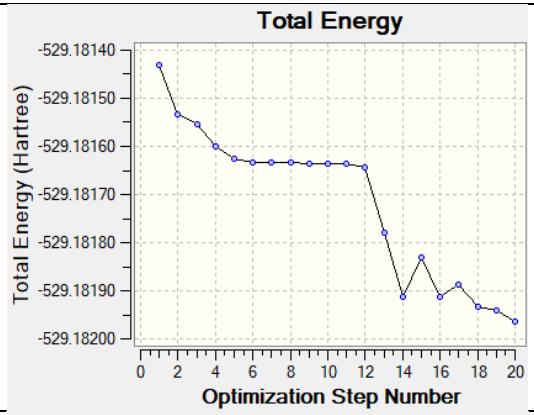
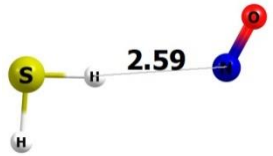
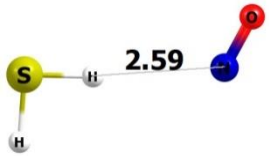
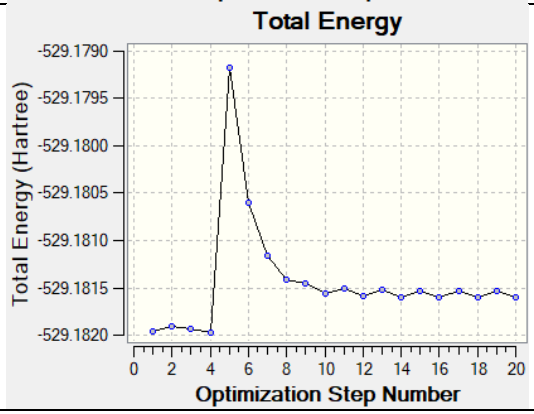
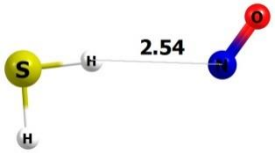
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S12	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S16 in the SI)**

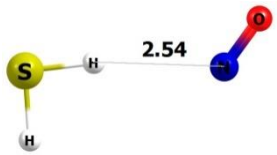
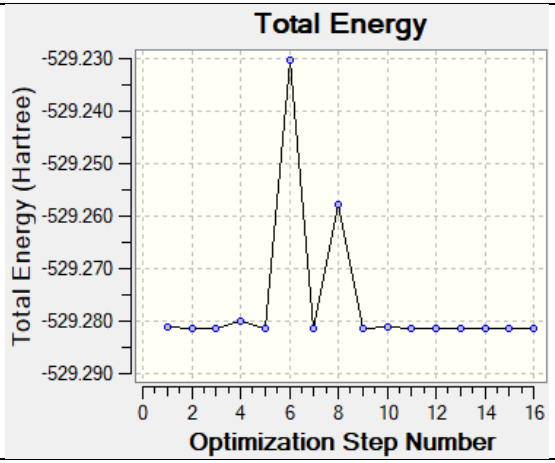
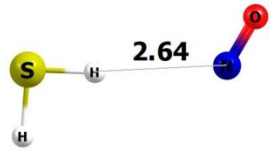
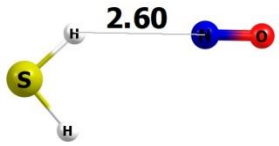
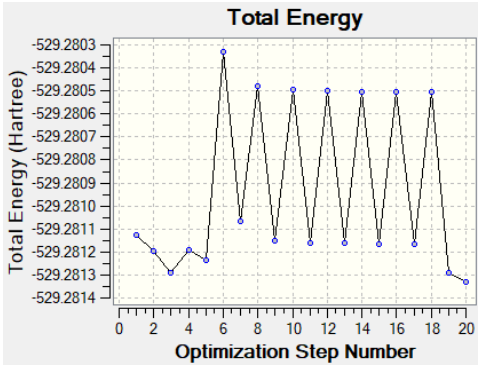
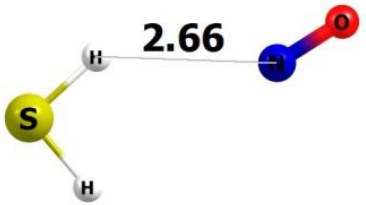
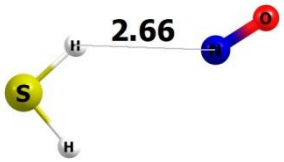
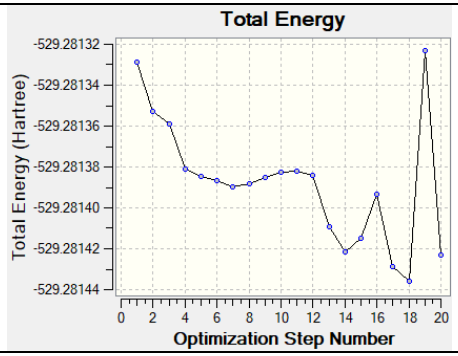
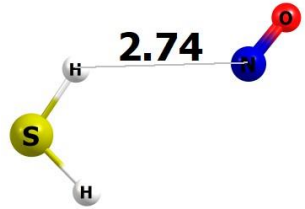
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S13	 **A Input Structure**		 Fully optimized minimum energy structure **B (S13 in the SI)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S14	 **A Input Structure**		 Fully optimized minimum energy structure **B (S14 in the SI)**
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S14	 **A Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

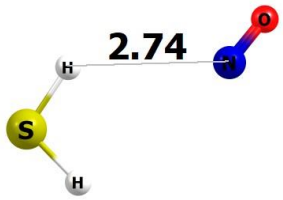
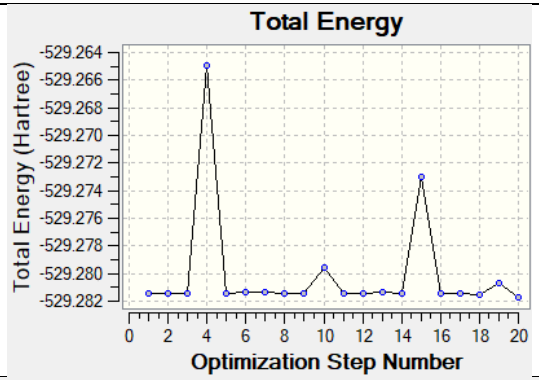
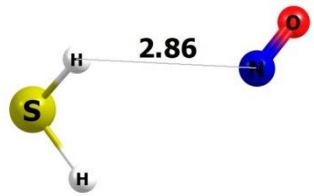
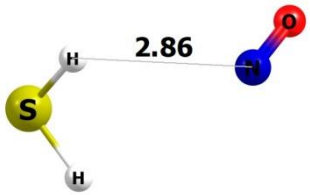
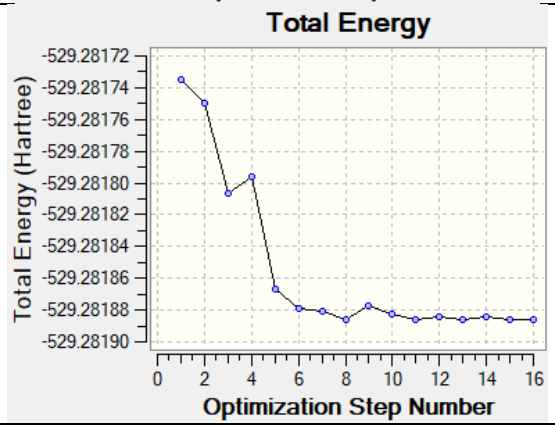
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S14 in the SI)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S15	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

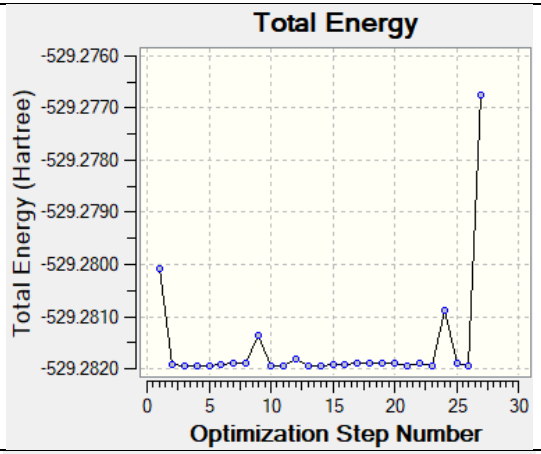
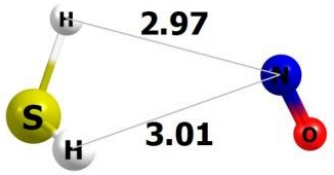
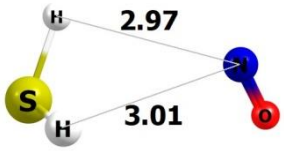
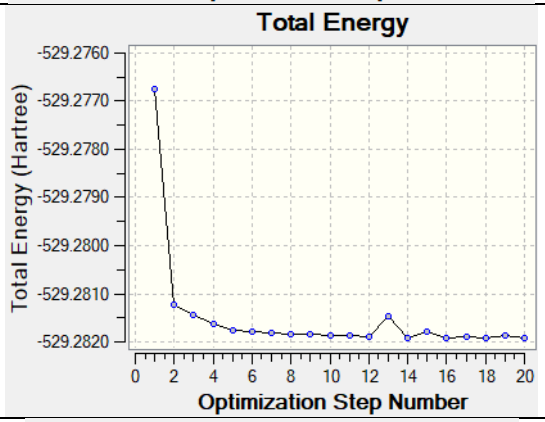
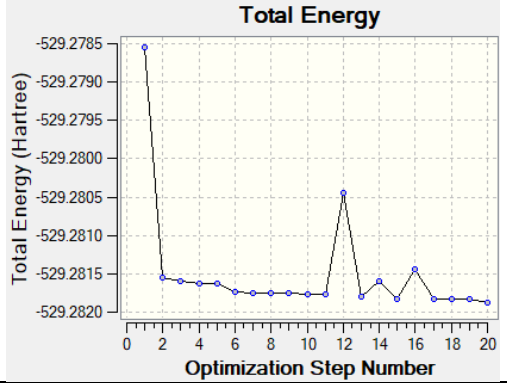
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E** (**S15 in the SI)**
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S15	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (having a positive interaction energy, not part of any figure in the paper)**

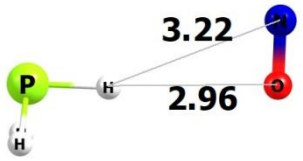
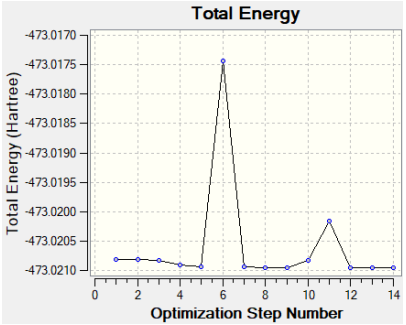
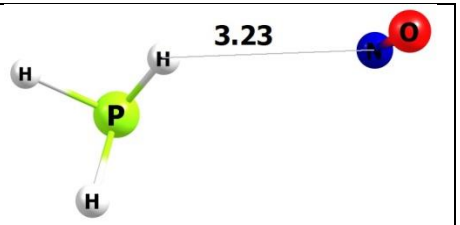
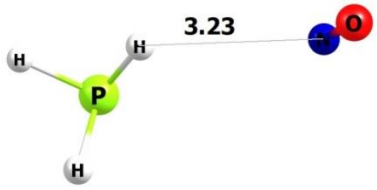
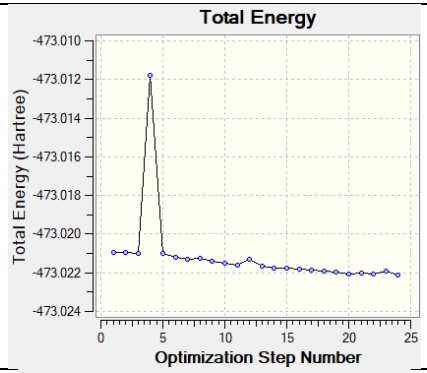
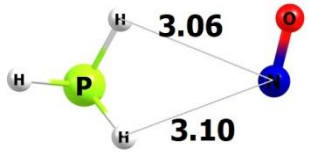
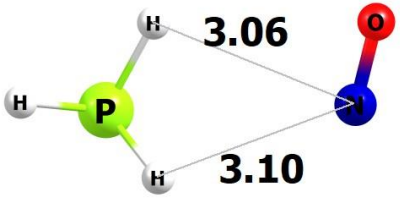
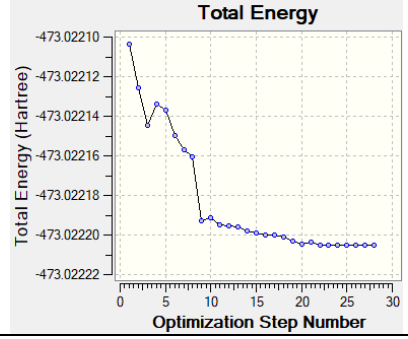
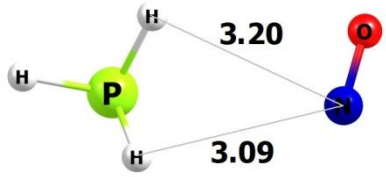
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S16	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S16 in the SI)**

NO · · · Molecules			
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S17	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S17 in the SI)**
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S17	 **A**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure)

			C
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**

	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 (Job ended without giving any optimized minimum energy structure) **E**
	 (Starting an optimization calculation with the same non-optimized geometry **F**)		 (Job ended without giving any optimized minimum energy structure) **F**
	 (Starting an optimization calculation with the same non-optimized geometry **G**)		 Fully optimized minimum energy structure **H (having a positive interaction energy, not part of any figure in the paper)**

Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S18	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D (S18 in the SI)**

<table>
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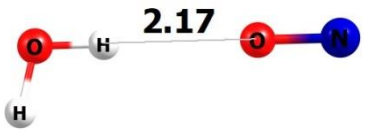
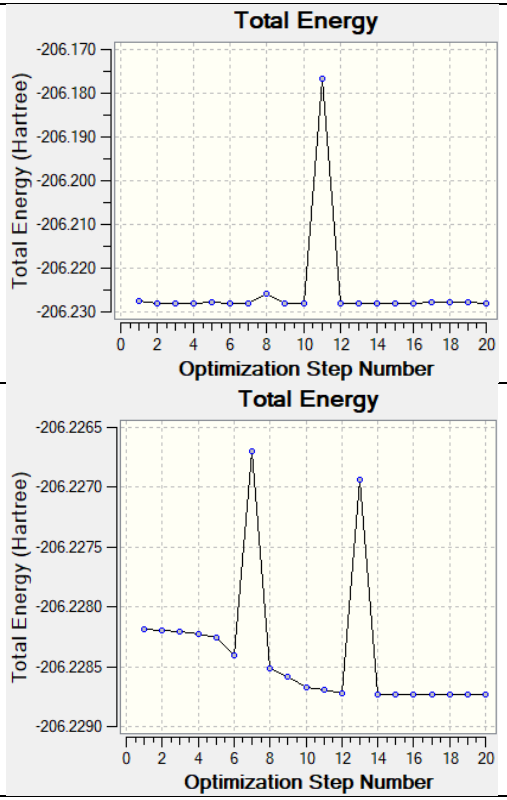
<td> 

A
Input Structure</td>
<td rowspan="2"> 
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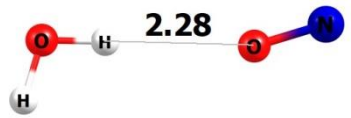
<td> 

(Job ended without giving any optimized minimum energy structure)
B</td>
</tr>
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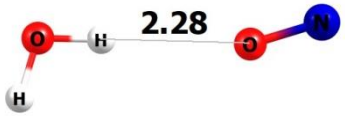
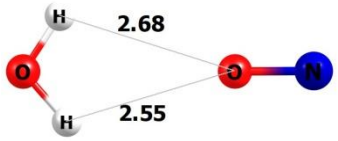
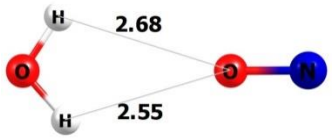
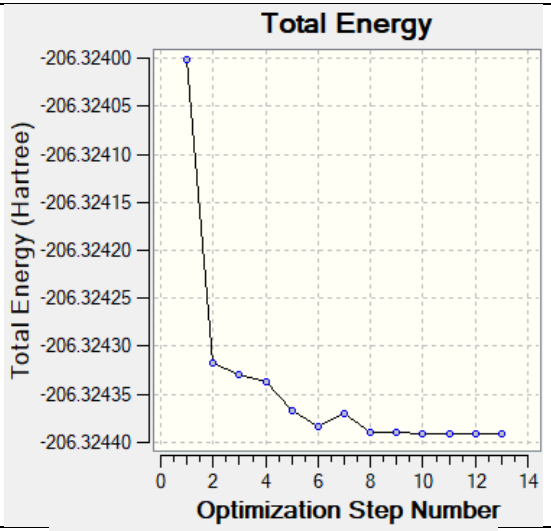
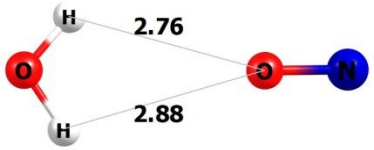
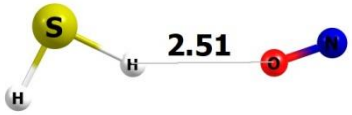
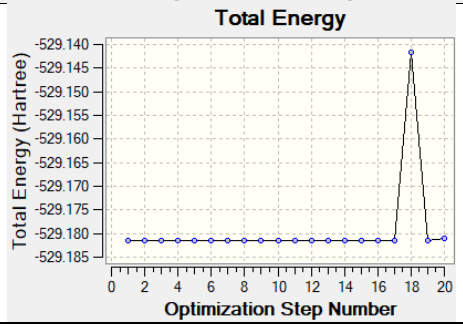
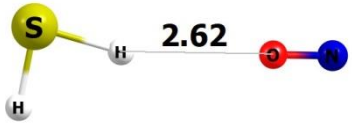
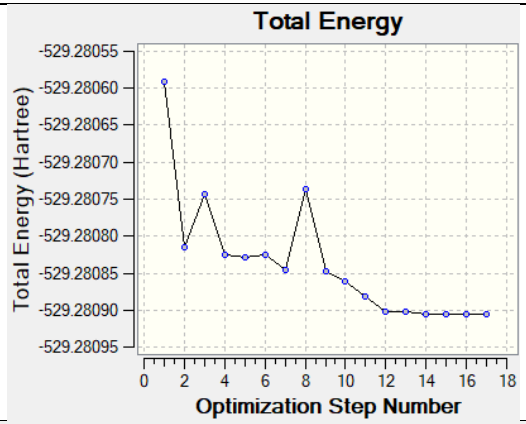
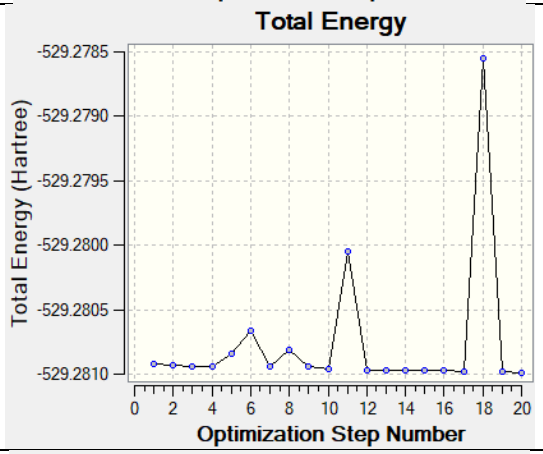
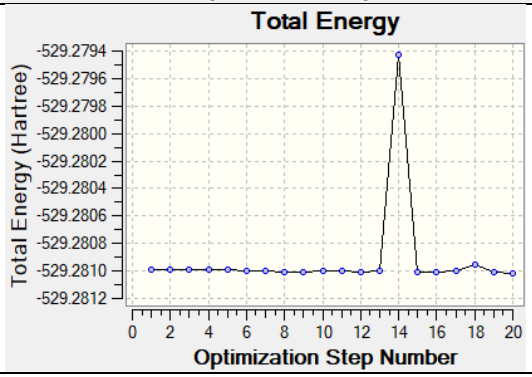
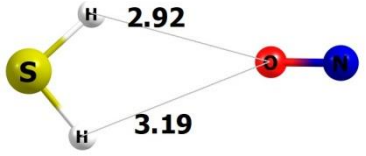
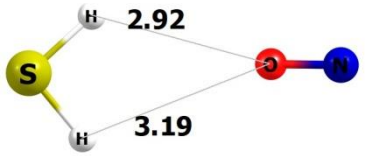
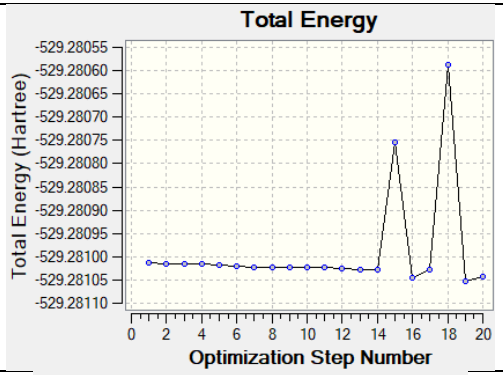
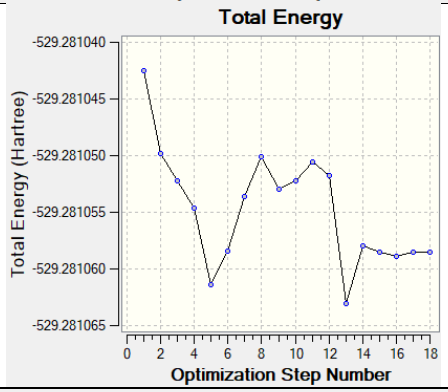
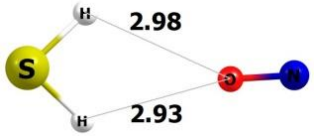
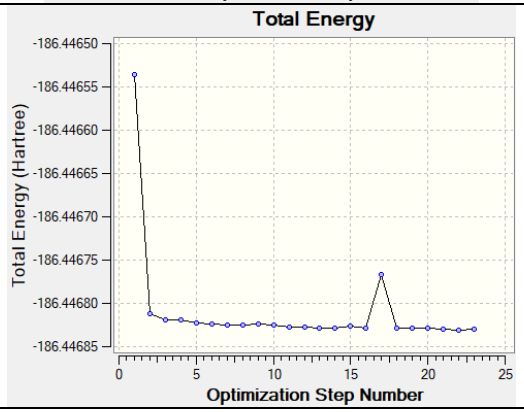
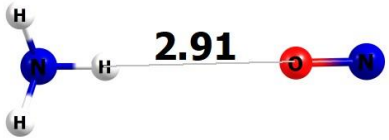
<td> 

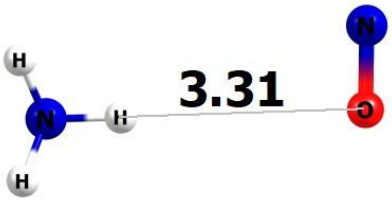
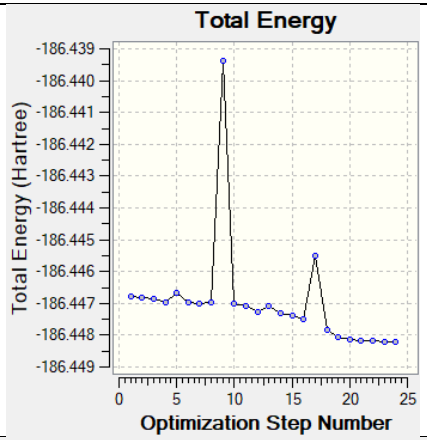
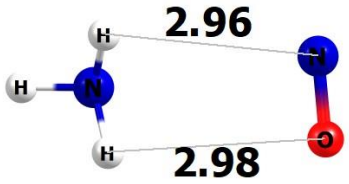
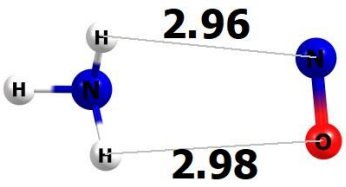
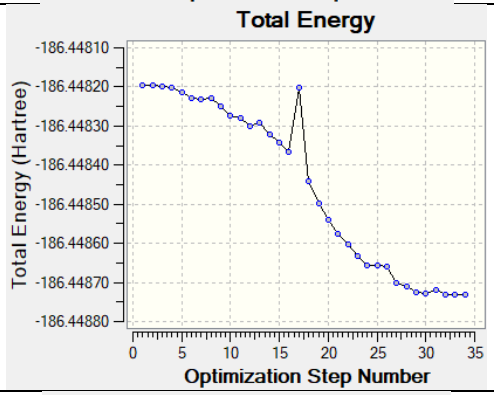
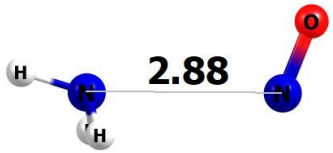
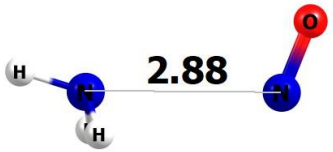
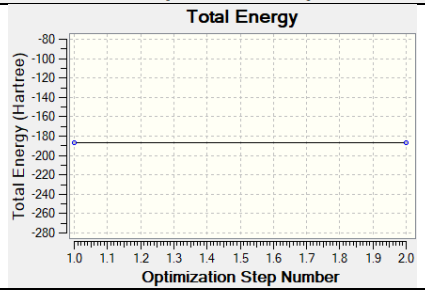
(Starting an optimization calculation with the same non-optimized geometry B)</td>
<td> 

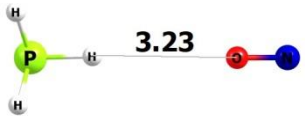
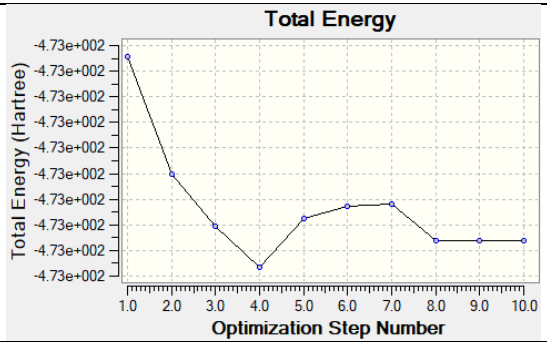
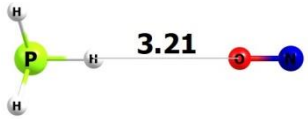
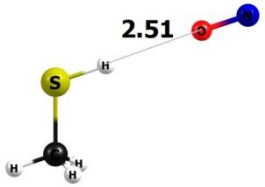
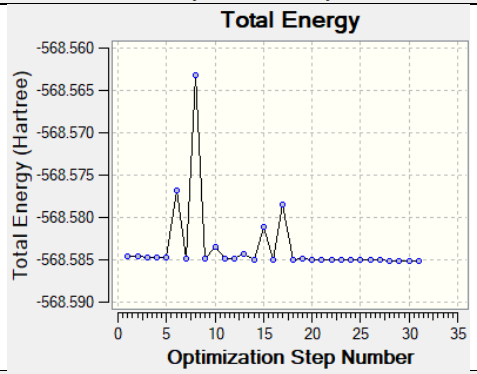
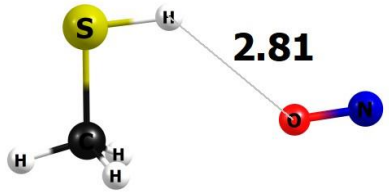
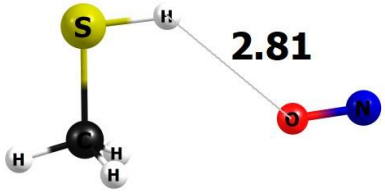
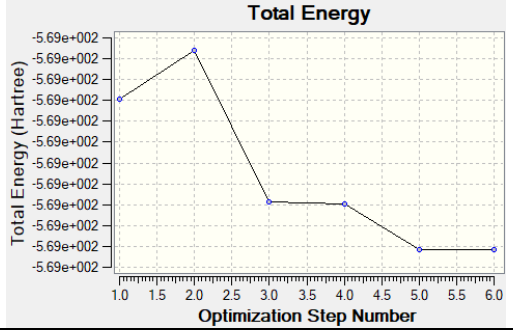
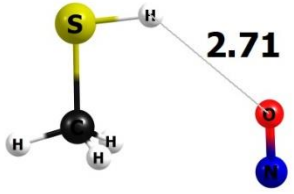
(Job ended without giving any optimized minimum energy structure)
C</td>
</tr>
</table>

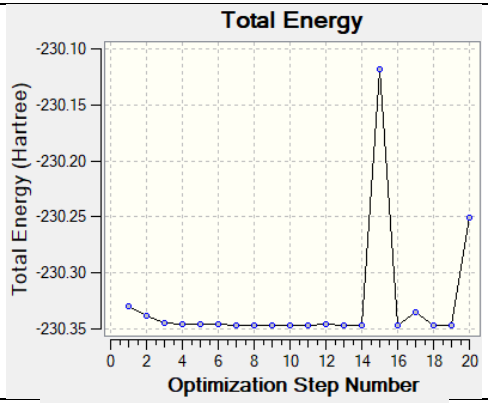
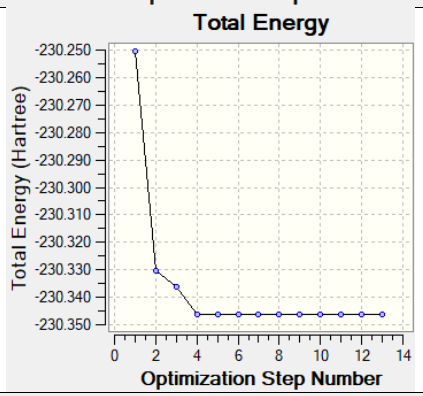
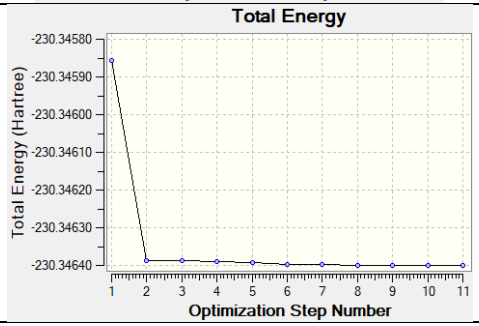
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S19 in the SI)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S20	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

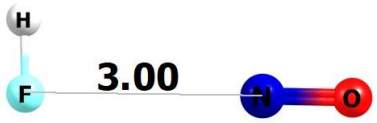
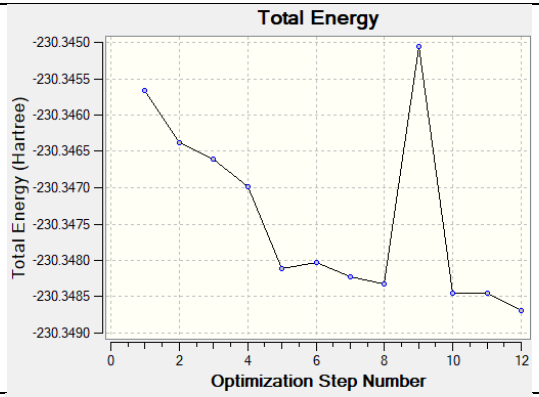
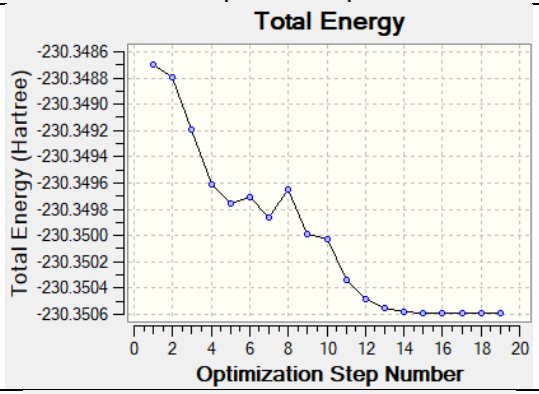
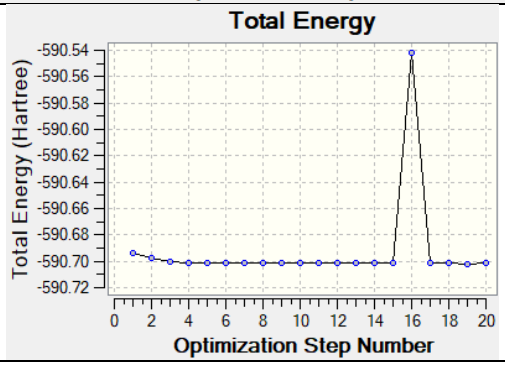
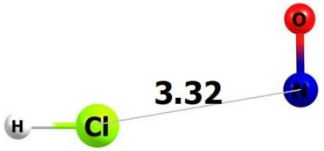
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S20 in the SI)**
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S20	 **A**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

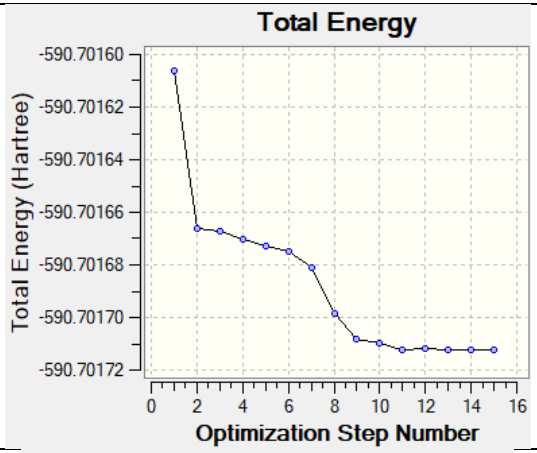
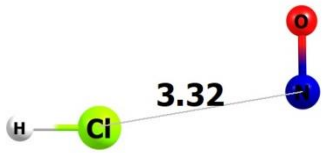
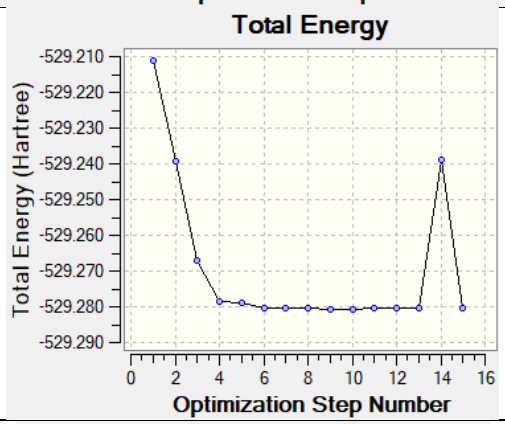
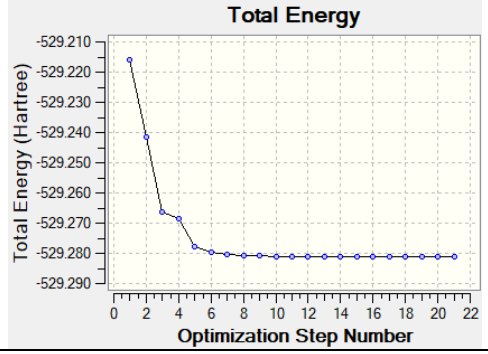
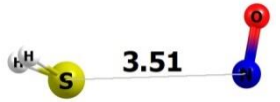
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E (having a positive interaction energy, not part of any figure in the paper)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S21	 **A** **Input Structure**		 Fully optimized minimum energy structure **B** (**S21 in the SI)**

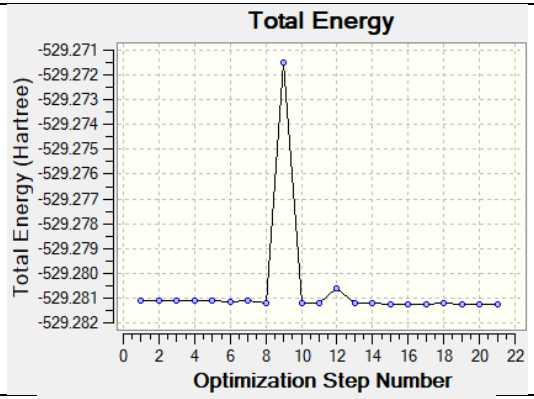
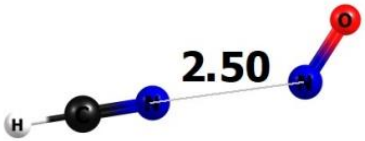
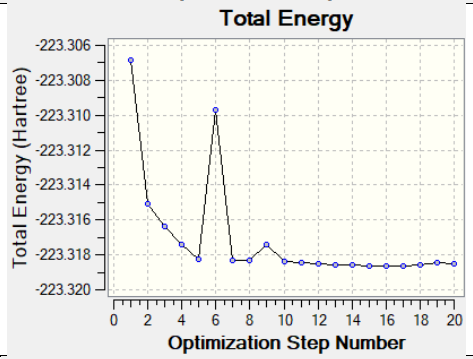
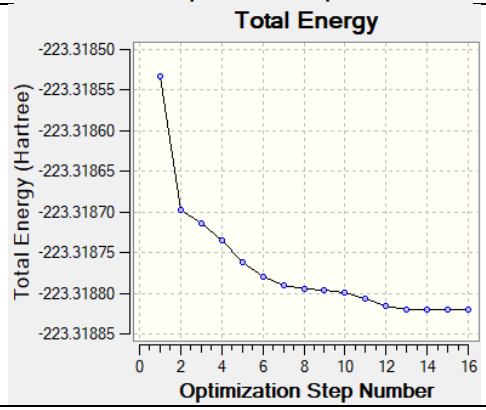
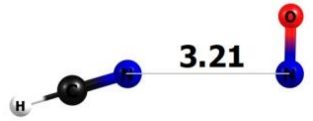
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S21	 **A**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**11h in the main text)**

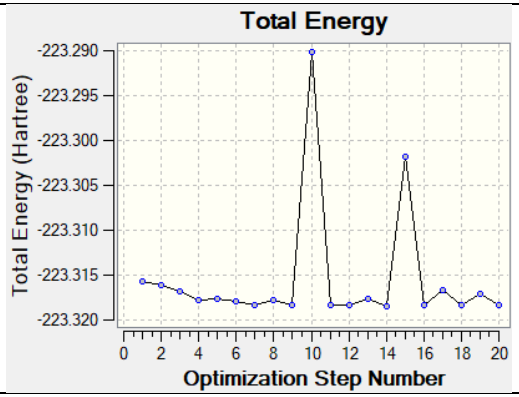
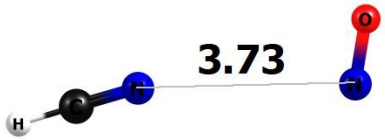
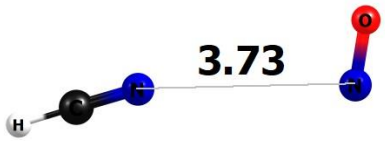
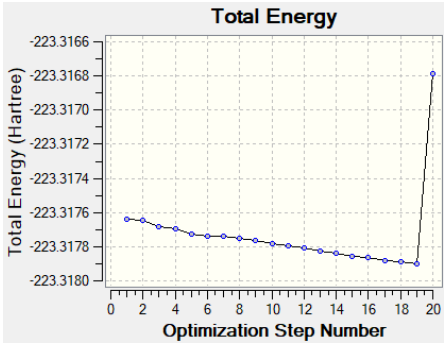
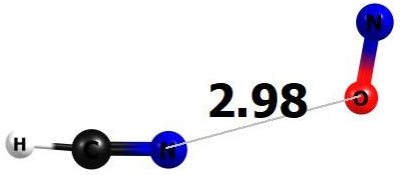
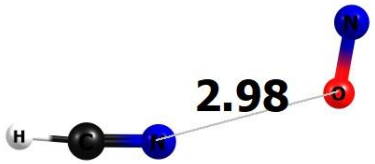
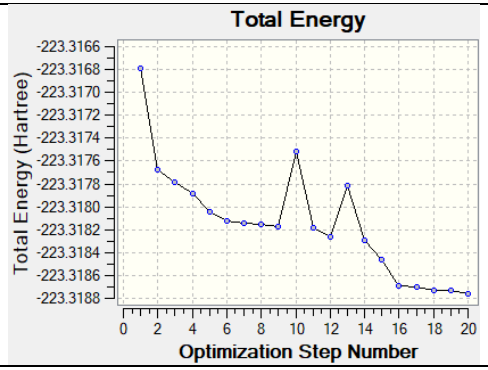
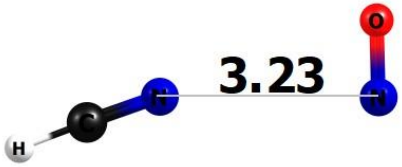
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S22	 **A Input Structure**		 Fully optimized minimum energy structure **B (S22 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S23	 **A Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C (S23 in the SI)**

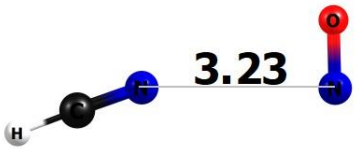
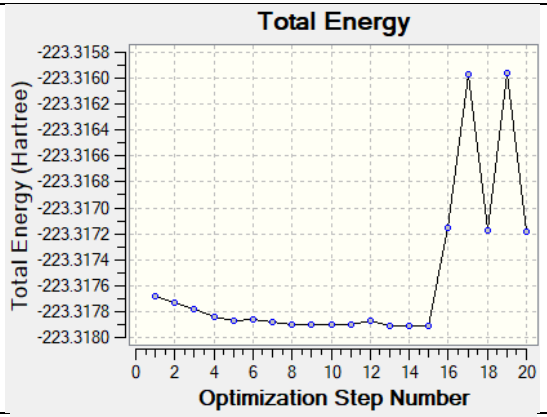
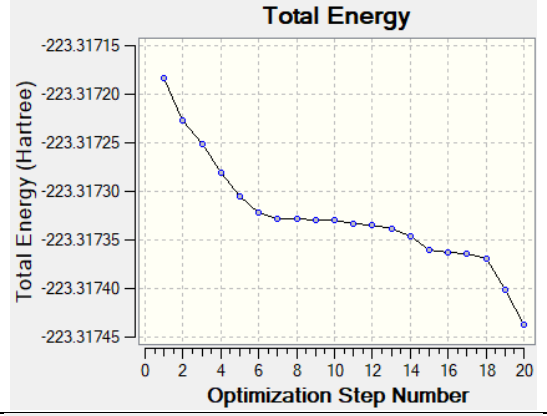
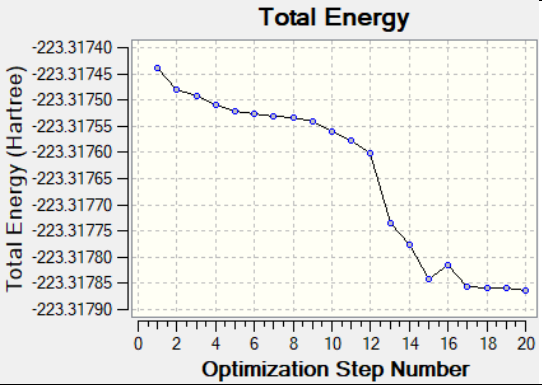
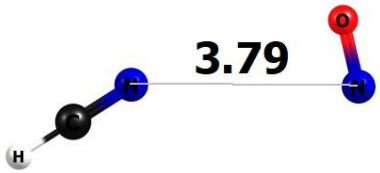
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S24	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D (S24 in the SI)**

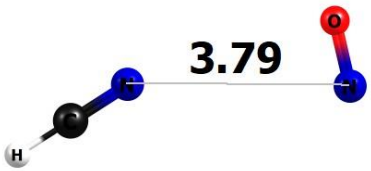
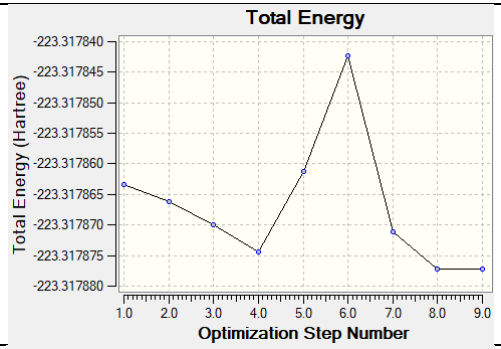
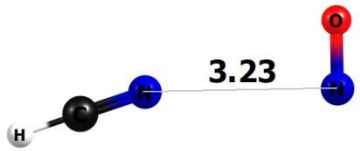
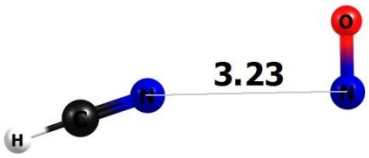
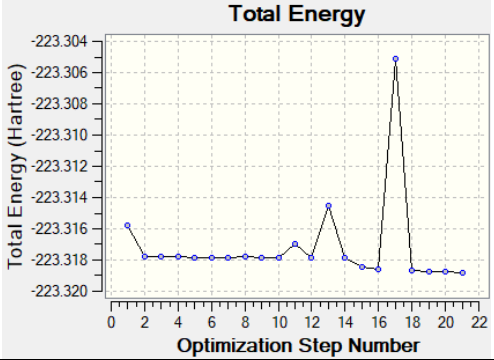
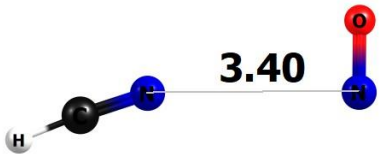
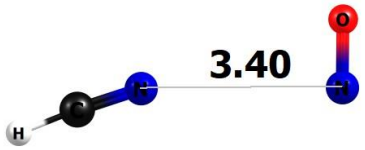
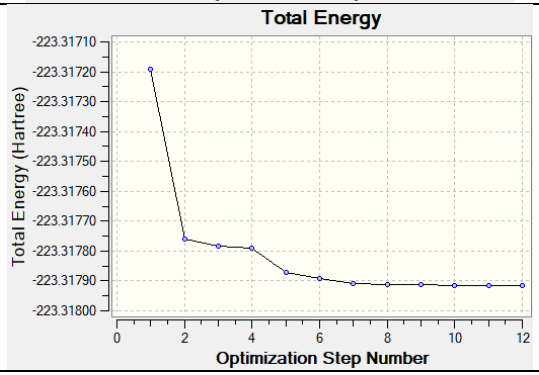
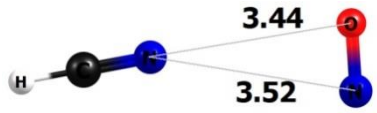
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S24	 **A Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C (10a in the main text)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S25	 **A Input Structure**		 Fully optimized minimum energy structure **B (S25 in the SI)**

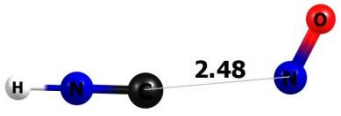
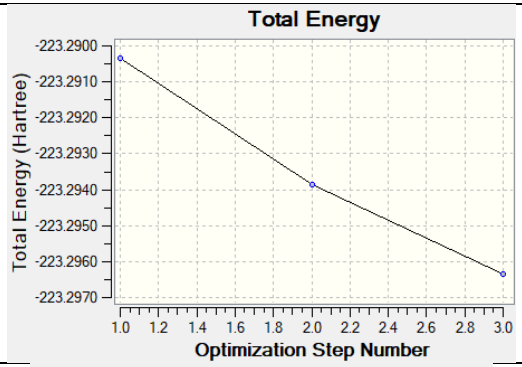
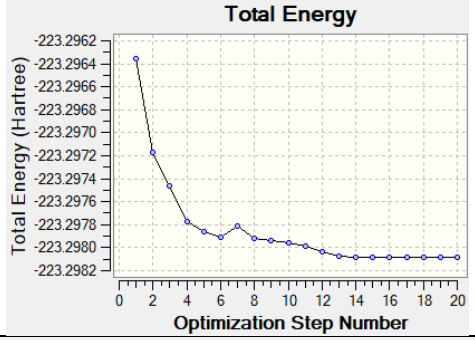
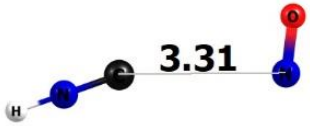
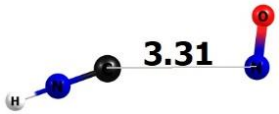
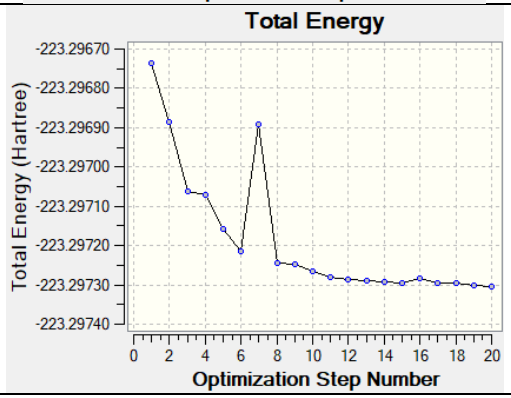
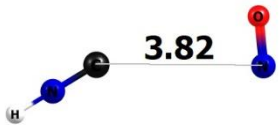
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S25	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (S25 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S26	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

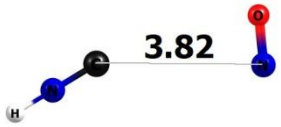
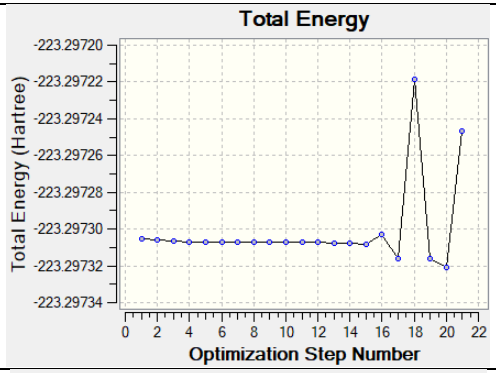
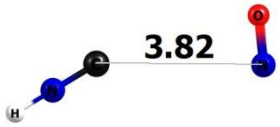
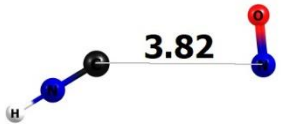
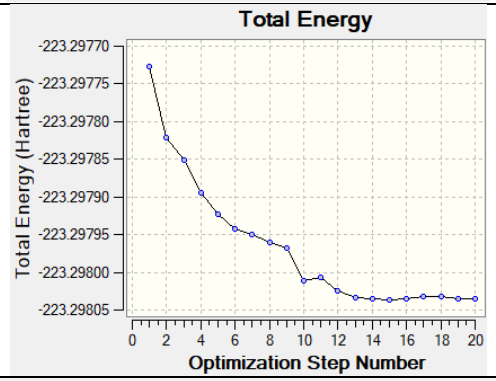
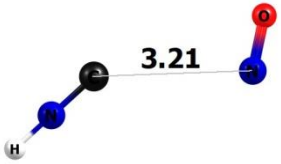
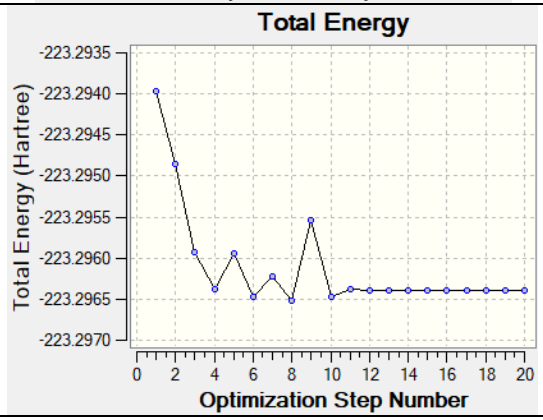
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S26 in the SI)**
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S27	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S27 in the SI)**

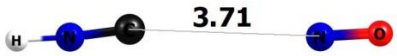
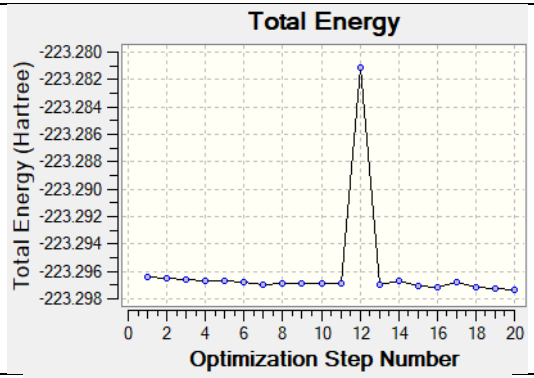
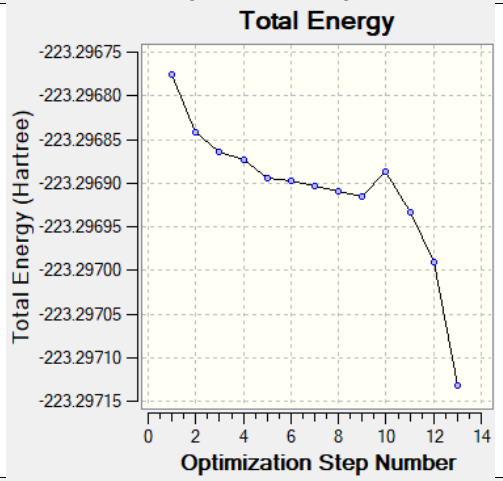
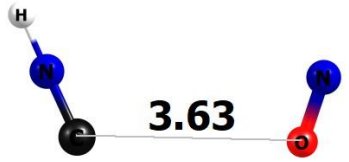
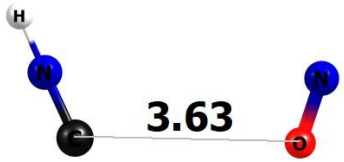
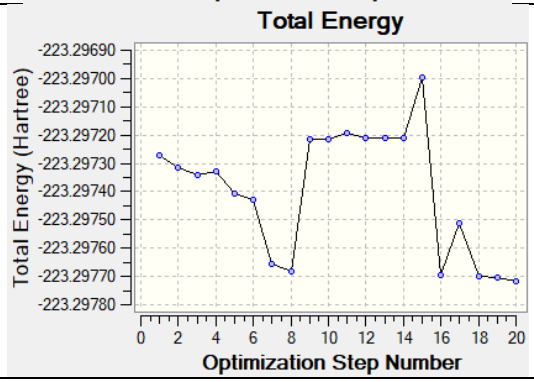
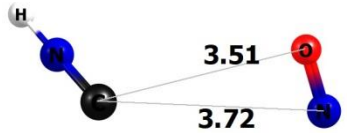
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S27	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**

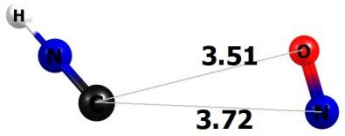
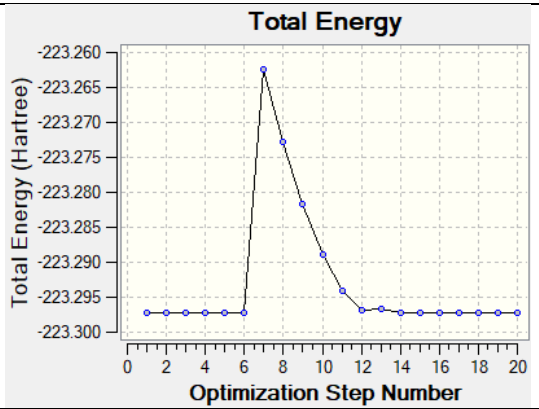
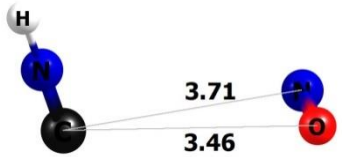
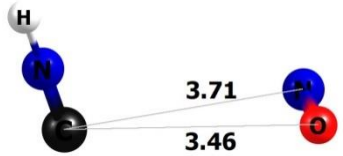
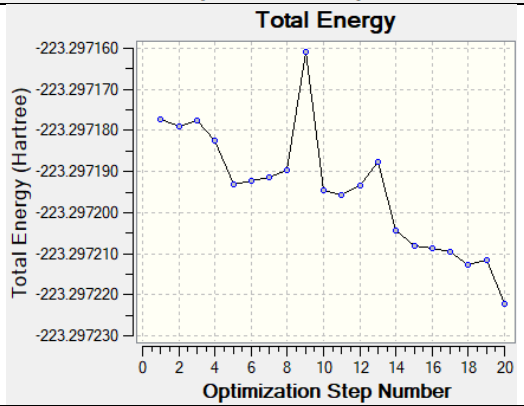
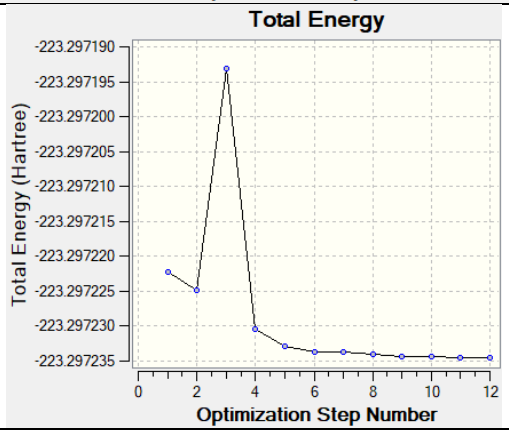
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**
	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 (Job ended without giving any optimized minimum energy structure) **F**
	 (Starting an optimization calculation with the same non-optimized geometry **F**)		 (Job ended without giving any optimized minimum energy structure) **G**

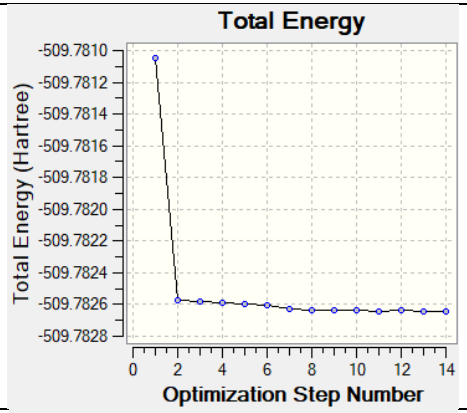
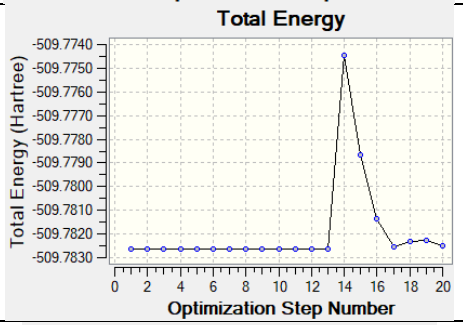
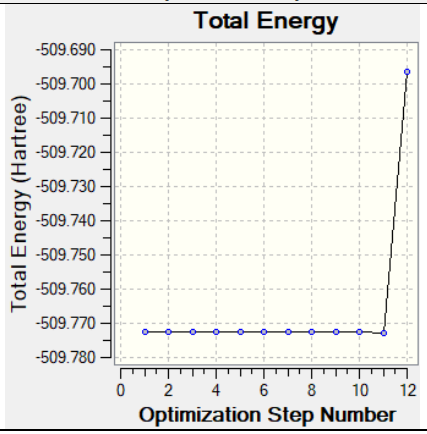
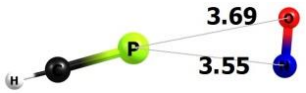
	 (Starting an optimization calculation with the same non-optimized geometry **G**)		 (Job ended without giving any optimized minimum energy structure) **H**
	 (Starting an optimization calculation with the same non-optimized geometry **H**)		 (Job ended without giving any optimized minimum energy structure) **I**
	 (Starting an optimization calculation with the same non-optimized geometry **I**)		 Fully optimized minimum energy structure **J (having a positive interaction energy, not part of any figure in the paper)**

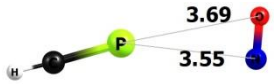
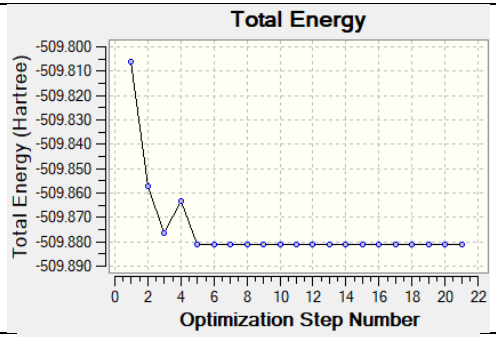
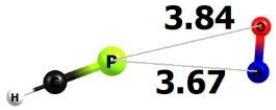
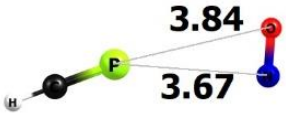
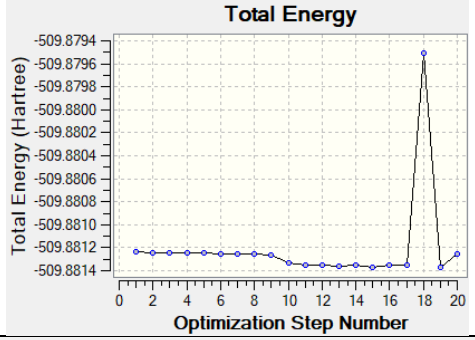
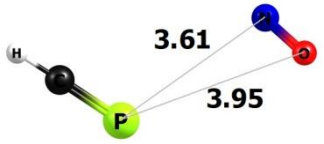
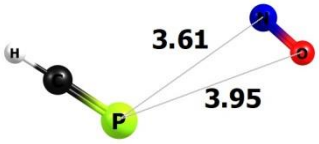
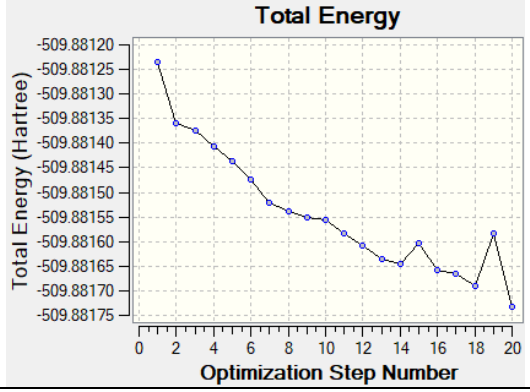
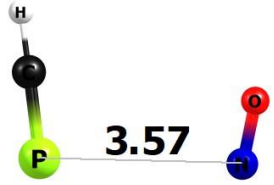
Attempt I to optimize an isomer/check for other electronic states alternate to the structure in Fig. S28	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**

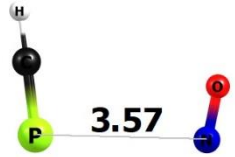
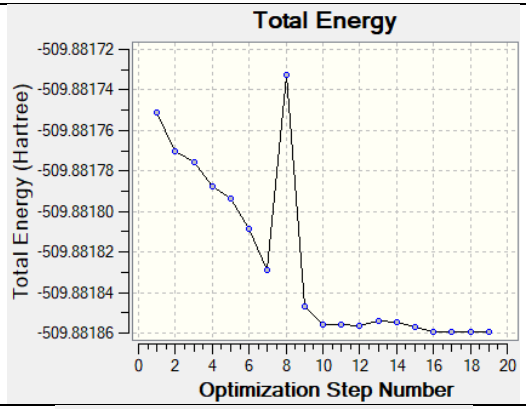
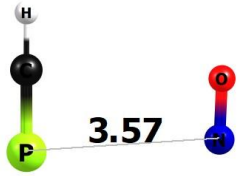
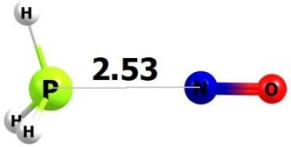
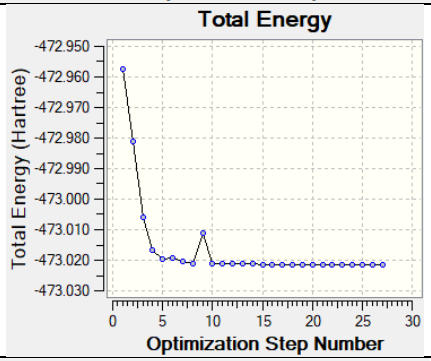
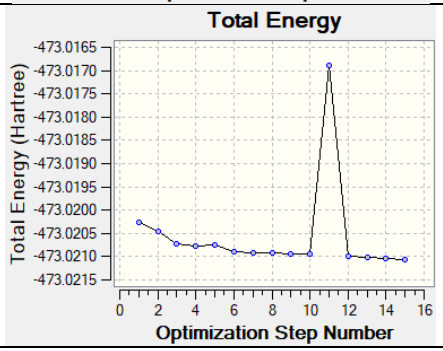
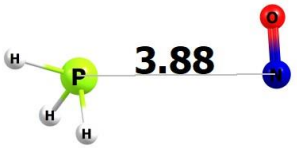
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**
	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 Fully optimized minimum energy structure **F (S28 in the SI)**
Attempt II to optimize an isomer/check for other electronic states alternate to the structure in Fig. S28	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

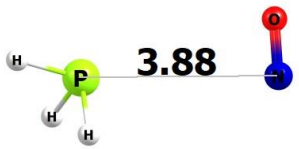
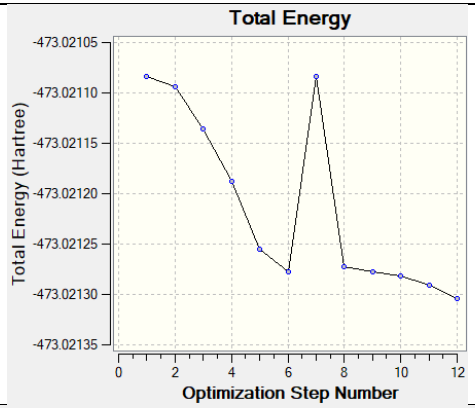
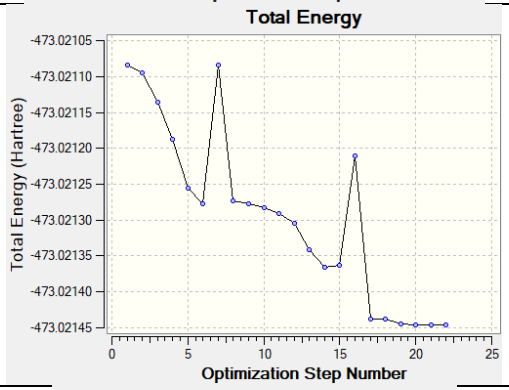
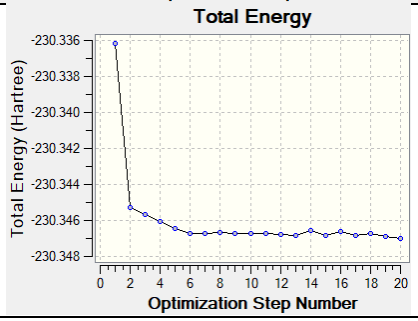
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**

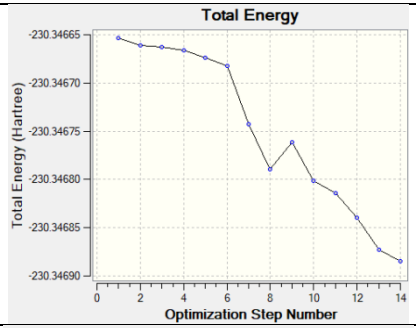
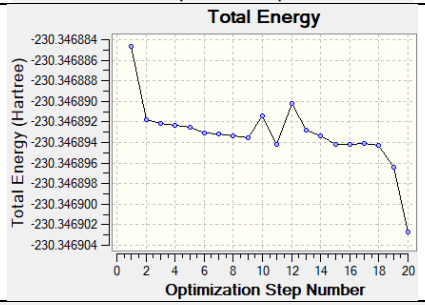
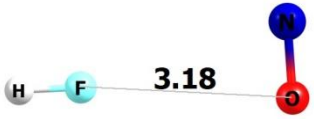
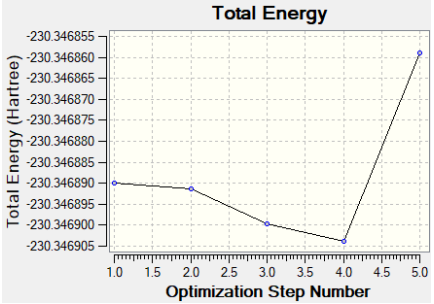
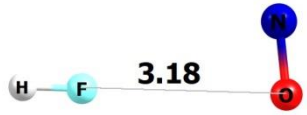
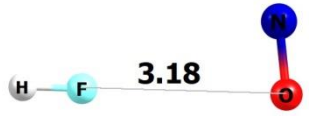
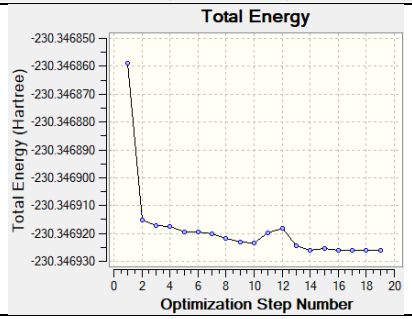
	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 (Job ended without giving any optimized minimum energy structure) **F**
	 (Starting an optimization calculation with the same non-optimized geometry **F**)		 (Job ended without giving any optimized minimum energy structure) **G**
	 (Starting an optimization calculation with the same non-optimized geometry **G**)		 Fully optimized minimum energy structure **H (having a positive interaction energy, not part of any figure in the paper)**

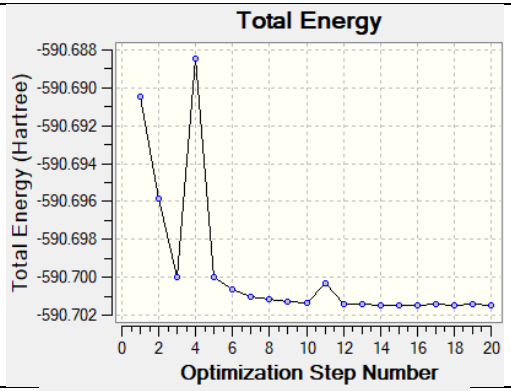
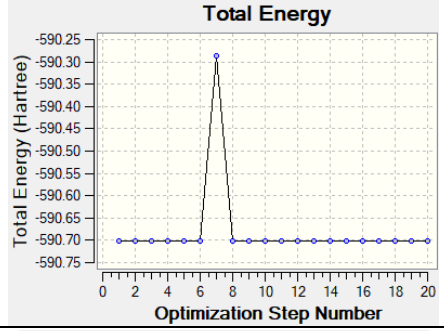
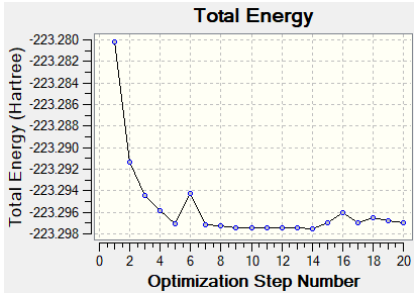
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S29	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**

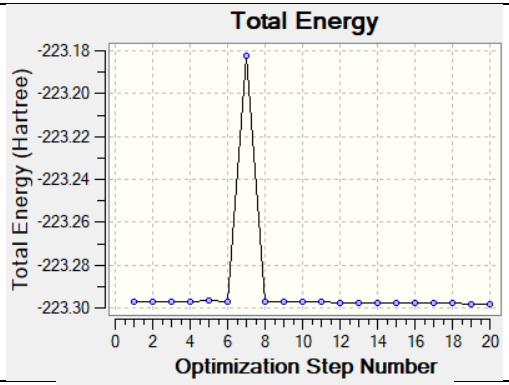
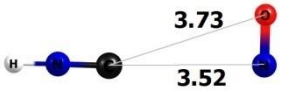
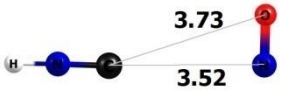
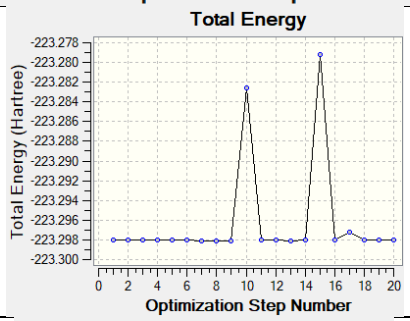
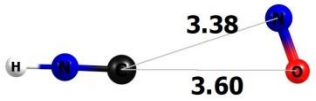
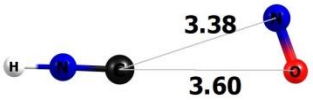
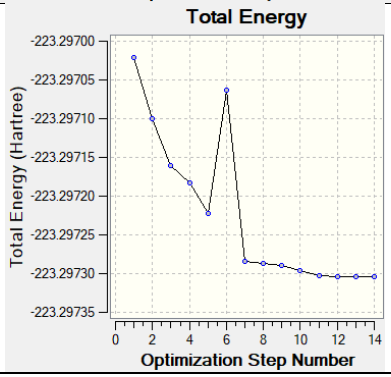
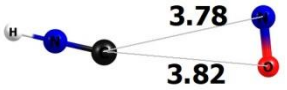
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**
	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 (Job ended without giving any optimized minimum energy structure) **F**
	 (Starting an optimization calculation with the same non-optimized geometry **F**)		 (Job ended without giving any optimized minimum energy structure) **G**

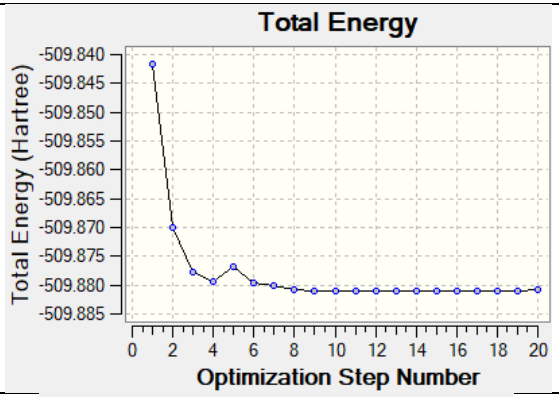
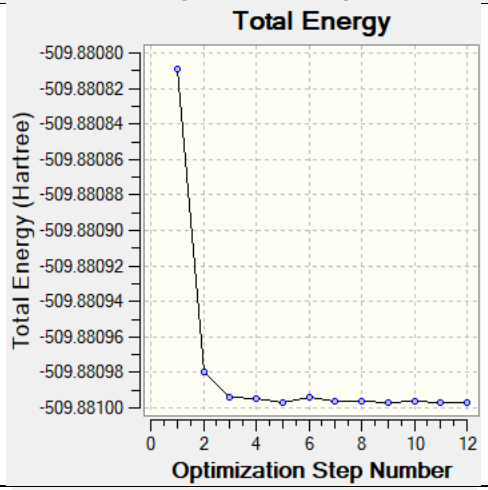
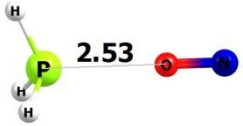
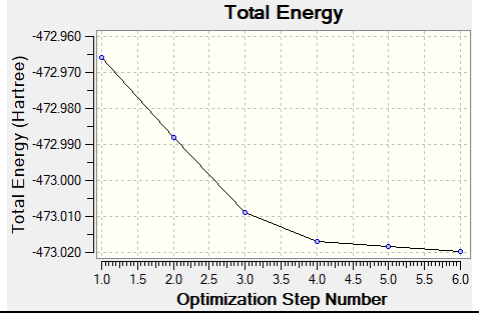
	 (Starting an optimization calculation with the same non-optimized geometry **G**)		 Fully optimized minimum energy structure **H (S29 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S30	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

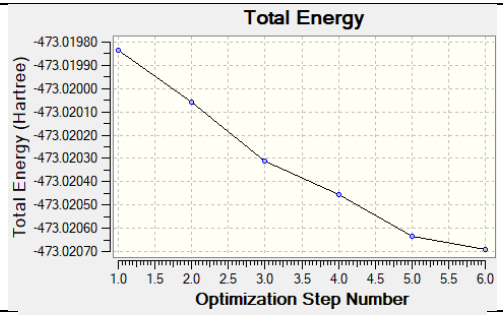
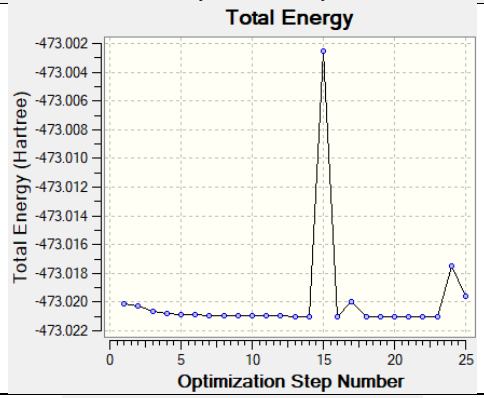
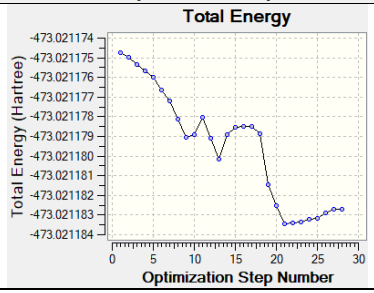
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E** (**S30 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S31	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

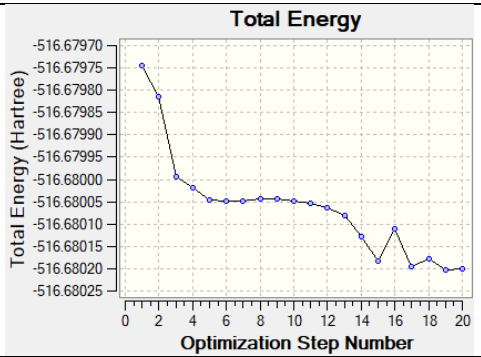
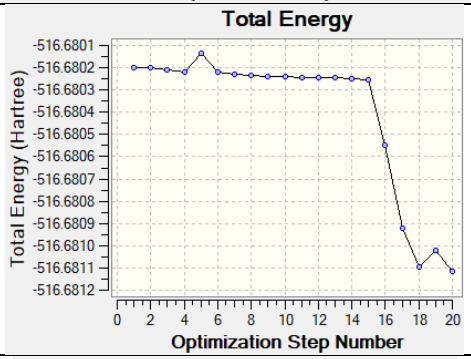
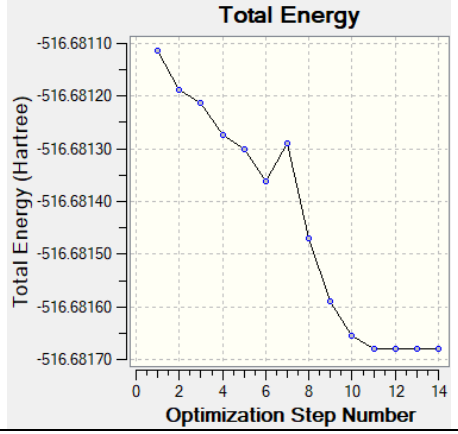
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 (Job ended without giving any optimized minimum energy structure) **E**
	 (Starting an optimization calculation with the same non-optimized geometry **E**)		 Fully optimized minimum energy structure **F (S31 in the SI)**

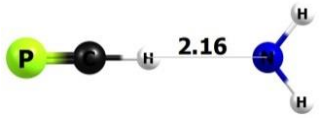
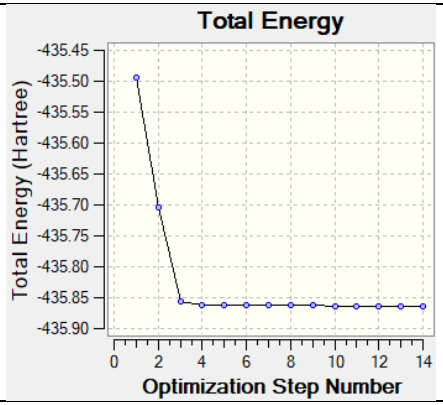
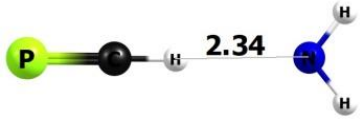
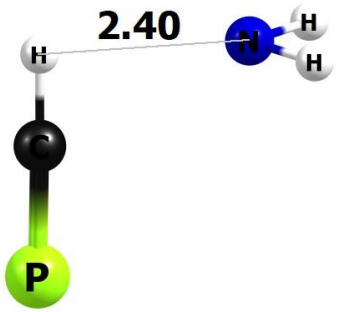
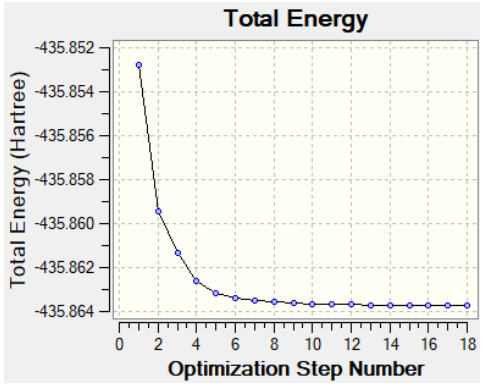
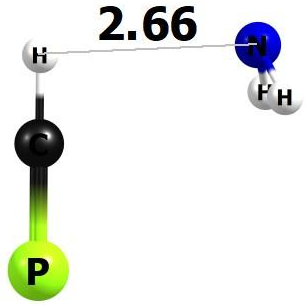
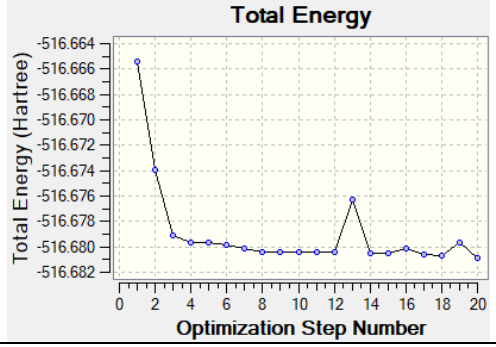
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S32	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S32 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S33	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

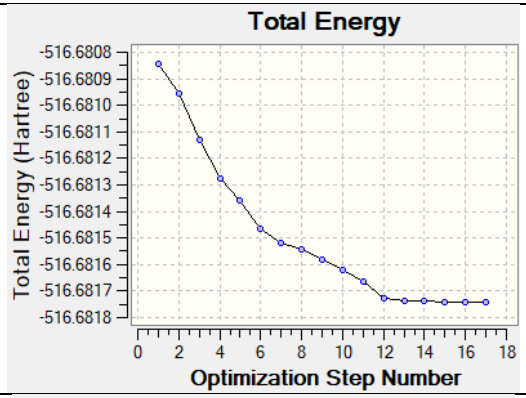
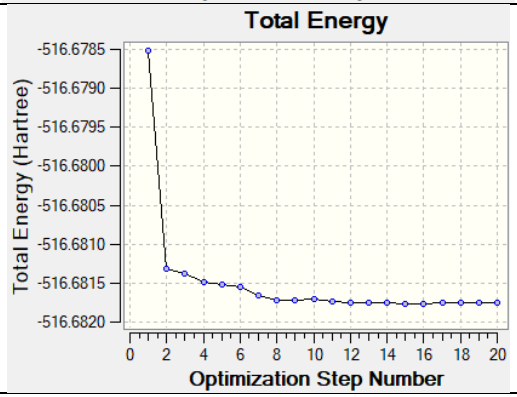
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E (S33 in the SI)**

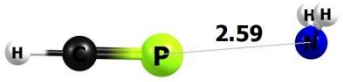
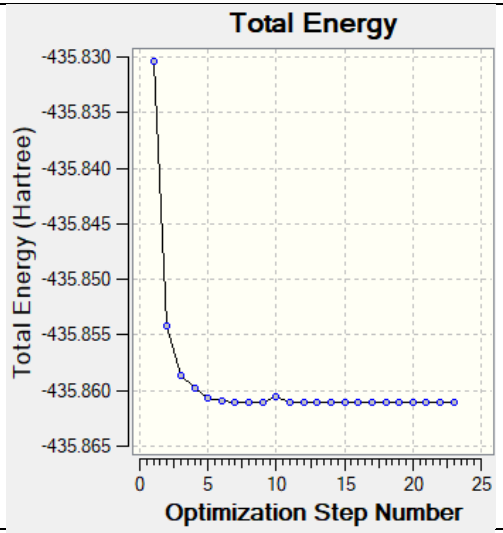
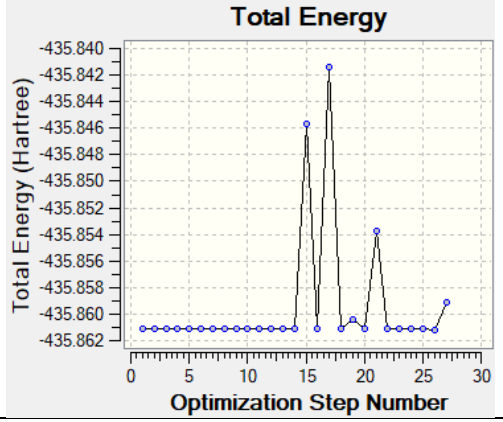
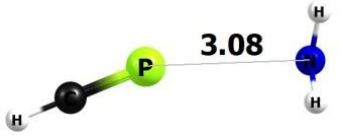
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S34	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S34 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S35	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

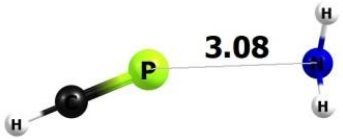
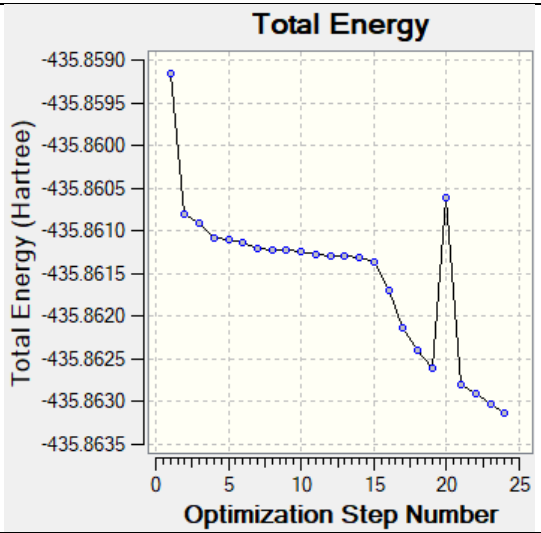
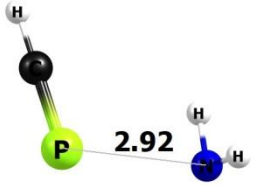
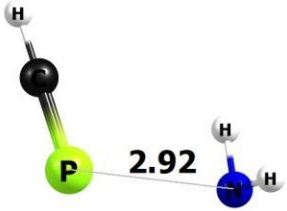
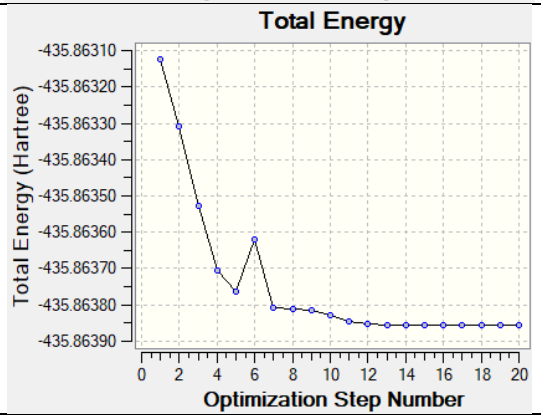
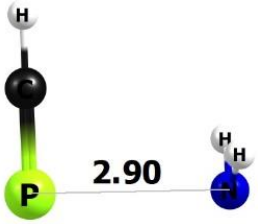
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E** (**S35 in the SI)**
$NH_2\cdots$Molecules			

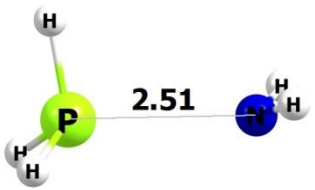
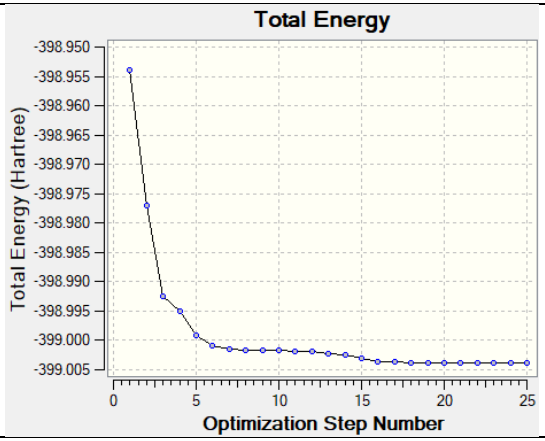
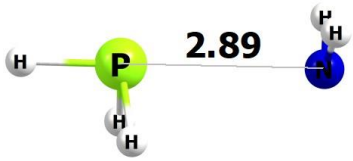
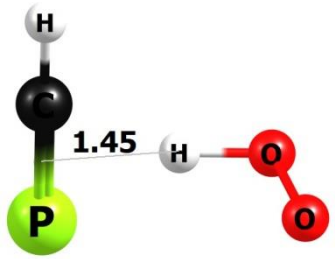
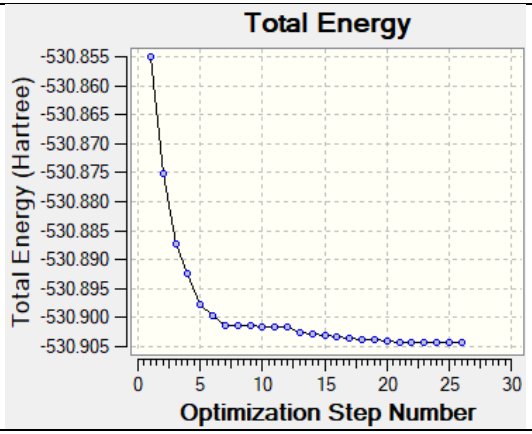
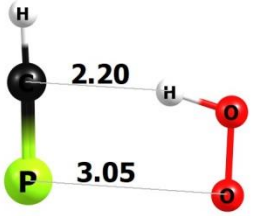
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S36	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D (S36 in the SI)**

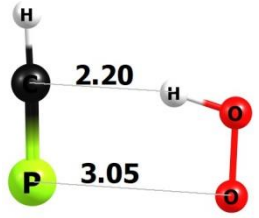
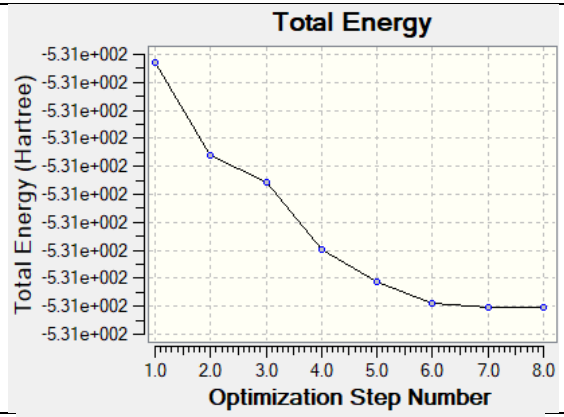
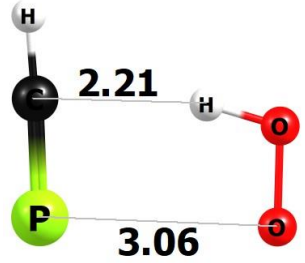
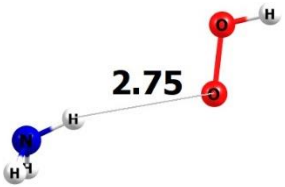
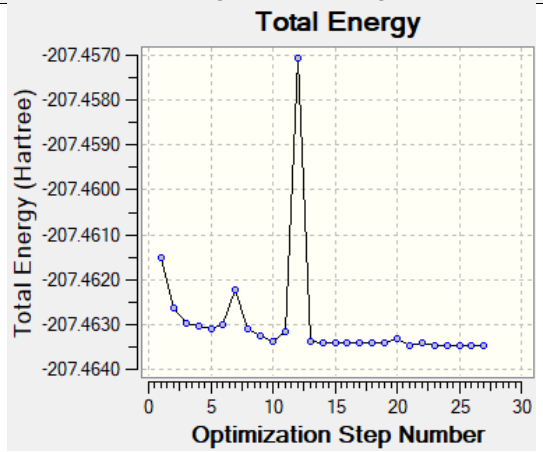
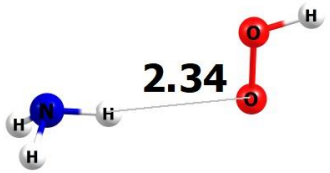
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S37	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (S37 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. 13g ***New Isomer having lower interaction energy found***	 **A** **Input Structure**		 Fully optimized minimum energy structure **B (13g in the main text)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S38	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

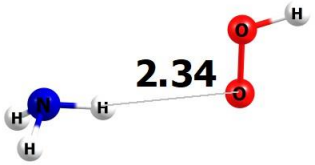
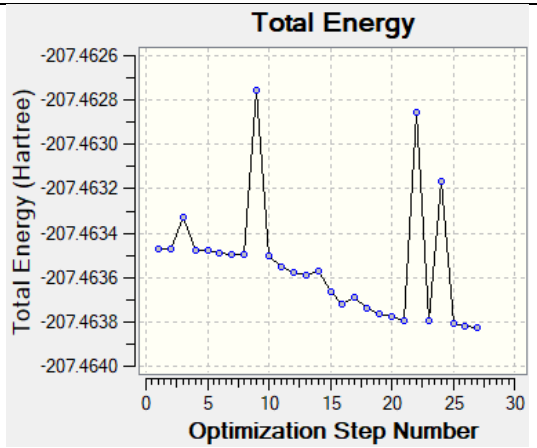
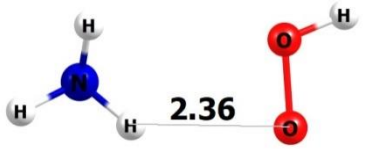
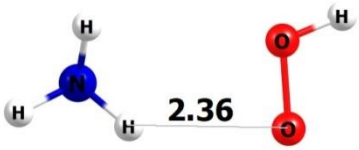
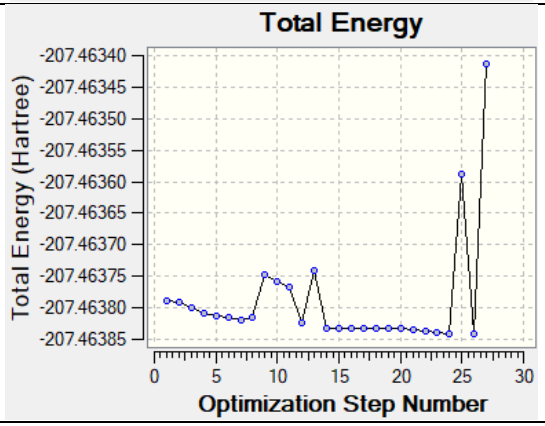
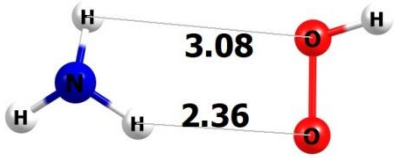
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 Fully optimized minimum energy structure **D** (**S38 in the SI)**

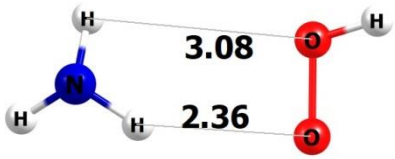
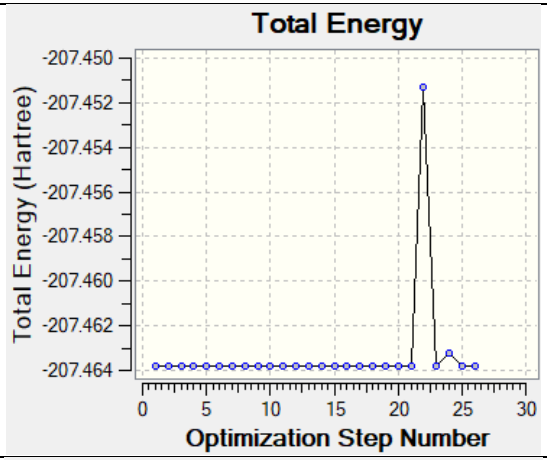
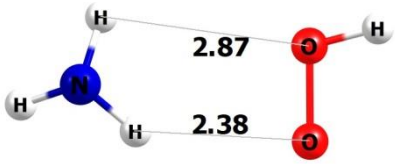
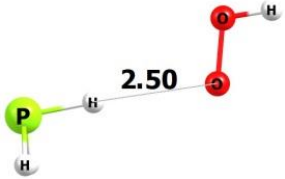
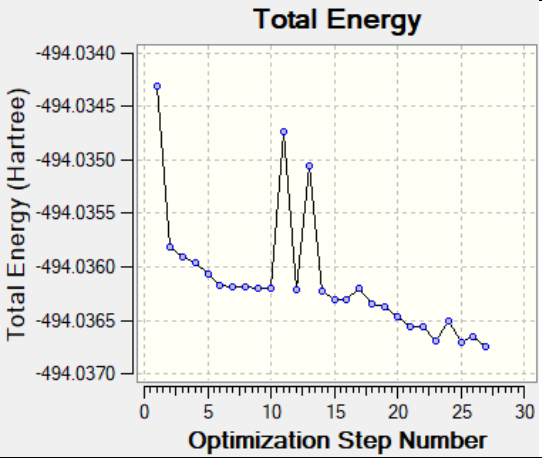
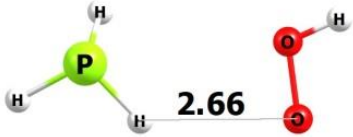
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S39	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**
	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**

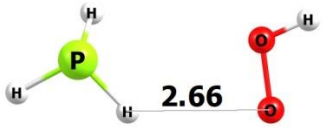
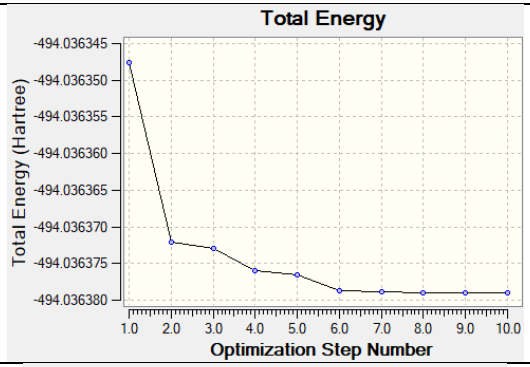
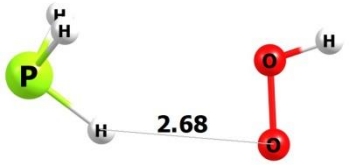
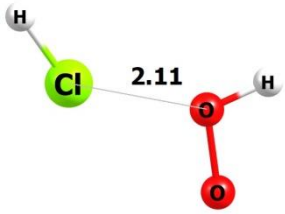
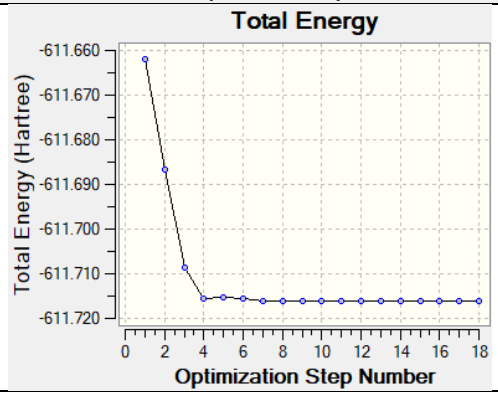
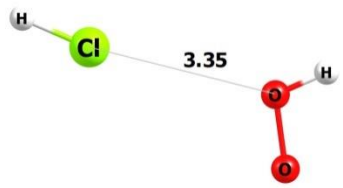
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**
	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E (S39 in the SI)**

Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S40	 **A Input Structure**		 Fully optimized minimum energy structure **B (S40 in the SI)**
$HO_2\cdots$Molecules			
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. 15h ***New Isomer having lower interaction energy found***	 **A Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**15h in the main text)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S41	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 (Job ended without giving any optimized minimum energy structure) **C**
	 (Starting an optimization calculation with the same non-optimized geometry **C**)		 (Job ended without giving any optimized minimum energy structure) **D**

	 (Starting an optimization calculation with the same non-optimized geometry **D**)		 Fully optimized minimum energy structure **E** (**S41 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S42	 **A** **Input Structure**		 (Job ended without giving any optimized minimum energy structure) **B**

	 (Starting an optimization calculation with the same non-optimized geometry **B**)		 Fully optimized minimum energy structure **C** (**S42 in the SI)**
Attempt to optimize an isomer/check for other electronic states alternate to the structure in Fig. S43	 **A** **Input Structure**		 Fully optimized minimum energy structure **B** (**S43 in the SI)**

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