

Supporting Information for

Photoactivation of Metal Halogen Bonds in a Ni(II) NHC Complex

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Preparation of Compounds

General Considerations. All synthetic manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere, or in a glovebox under an atmosphere of nitrogen. Reactions were carried out in oven-dried glassware cooled under vacuum. Elemental analysis was performed by Midwest Microlab, LLC, Indianapolis, IN. Toluene, THF, Et₂O and hexanes were purified by passing them under argon pressure through packed columns of neutral alumina. NMR solvents were obtained from Cambridge Isotope Laboratories. C₆D₆ was degassed, and stored in a glovebox over molecular sieves.

¹H NMR spectra were recorded on Varian 300 MHz instruments, with shifts reported relative to the residual solvent peak. UV-vis spectra were recorded on a Varian Cary 5000 spectrophotometer and Spectral Instruments 400 series diode array spectrometer. Spectra were referenced against the appropriate solvent. GC measurements were performed with an Agilent 7890A GC.

[Ni(IPr)]₂¹ and [Ni(μ-Cl)(IPr)]₂² were synthesized as described by published procedures. 2,6-lutidine·HCl was prepared by treatment of 2,6-lutidine with 1.0 M HCl diethyl ether solution under anhydrous conditions. A 1,4-dioxane solution of 4.0 M HCl (Aldrich), 2,6-lutidine (Aldrich) and 1,4-dimethoxybenzene (Aldrich) were used as received.

Preparation of [Ni(μ-Cl)Cl(IPr)]₂ (1). The title compound was prepared by oxidation of [Ni(μ-Cl)(IPr)]₂ with *N*-chlorosuccinimide as described in published procedure.³ Unlike previous reports, dichloromethane was avoided because of the potential of residual solvent reacting with the compounds. The crude product was recrystallized from a toluene solution layered with hexanes at -40 °C for 3 d. The supernatant was decanted from purple crystals, which were washed several times with hexanes to remove powder. The recrystallization was repeated two or three times. The ¹H NMR spectrum obtained for the compound reported here in benzene and in toluene is similar to that reported for the compound dissolved in toluene.³ Also, unit cell data of single crystals for crystals grown in the solvent system of DCM/pentane is similar to that previously reported.³ Compound **1** in solution is not stable for prolonged periods of time at room temperature even in the glove box unless the container is sealed. Thus, solutions of the complex should be prepared just prior handling. ¹H NMR (C₆D₆, 300 MHz): δ 13.72 (br), 5.96 (t, br), 5.75 (br), 4.49 (d, br), -1.55 (br). Anal. Calcd. C₅₄H₇₂N₄Cl₄Ni₂: C, 62.58; H, 7.00; N, 5.41. Found: C, 62.61; H, 6.99; N, 5.47. λ_{max} /nm (ε / 10³ M⁻¹ cm⁻¹) in toluene: 286 (4.8), 529 (0.3), 679 (0.1)

Preparation of [NiCl₂(IPr)(2,6-lutidine)] (2). In a glovebox, **1** (0.030 g, 0.0289 mmol) was added to a vial equipped with a Teflon-coated magnetic stirbar. The vial was charged with toluene and the mixture was stirred until all of compound was dissolved, after which 2,6-lutidine (0.0062 g, 0.0579 mmol) was added. Hexanes were layered on the resulting light

1 Lee, C. H.; Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 13802.

2 Dible, B. R.; Sigman, M. S.; Arif, A. M. *Inorg. Chem.* **2005**, *44*, 3772.

3 Laskowski, C.A.; Hillhouse, G. L. *Inorg. Chem.* **2009**, *48*, 6114.

pink solution, which was cooled to $-40\text{ }^{\circ}\text{C}$ overnight. The mixture was filtered through glass fiber to remove a white precipitate and the resulting solution was re-cooled at $-40\text{ }^{\circ}\text{C}$. The process was repeated until the white precipitate was not observed. The resulting light pink solution was concentrated and hexanes were added to the solution, which was cooled to $-40\text{ }^{\circ}\text{C}$ for 4 d. The supernatant was decanted and the resulting deep pink crystals were washed with hexanes. The resulting crystals were dried *in vacuo* to give 0.028 g (77%) of **2**. ^1H NMR (C_6D_6 , 300 MHz): δ 7.55–7.44 (m, 6 H, CH), 6.61 (s, 2 H, NCH), 6.38 (t, $J = 7.8$ Hz, 1 H, CH), 6.00 (d, $J = 7.9$ Hz, 2 H, CH), 3.51 (s, 6H, CCH_3), 3.32 (sept, $J = 6.9$ Hz, 4 H, $-\text{CH}(\text{CH}_3)_2$), 1.63 (d, $J = 6.6$ Hz, 12 H, $-\text{CH}(\text{CH}_3)_2$), 1.06 (d, $J = 7.0$ Hz, 12 H, $-\text{CH}(\text{CH}_3)_2$). Anal. Calcd. $\text{C}_{34}\text{H}_{45}\text{N}_3\text{Cl}_2\text{Ni}$: C, 65.30; H, 7.25; N, 6.72. Found: C, 64.84; H, 7.24; N, 6.76.

Experimental Methods

Photolysis of 1. Samples for all photolysis experiments were prepared in a nitrogen-filled glovebox in NMR tubes or Schlenk flasks. Photochemical reactions were performed at $10\text{ }^{\circ}\text{C}$ using a 1000 W high-pressure Hg/Xe arc lamp (Oriel) as an excitation source. The beam was passed through a water-jacketed filter holder containing appropriate long pass filters, an iris and collimating lens. The photolysis was deemed complete upon a solution color change from purple to greenish yellow with concomitant precipitation of an insoluble impurity that results from photolysis. After removing volatile materials, the resulting solid and 1,4-dimethoxybenzene were dispersed in C_6D_6 and the yields of the products were determined by NMR. Photolysis spectra are shown in Figure 2.

Treatment of $[\text{Ni}(\text{IPr})_2$ with HCl•dioxane. In a glovebox, $[\text{Ni}(\text{IPr})_2$ (0.030 g, 0.0335 mmol) was added to a vial equipped with a Teflon-coated magnetic stirbar; the vial was charged with toluene. And residual solid, if present, was removed by filtration. The solution was transferred to a Schlenk flask and was sealed with septa. 4.0 M HCl•dioxane solution (16.8 μL , 0.0672 mmol HCl) was added via syringe. The mixture was stirred for ~ 1 h. The headspace gas was analyzed by GC. After removing volatile materials, the resulting solid and 1,4-dimethoxybenzene were dispersed in C_6D_6 and the yields of the products were determined by NMR.

Treatment of $[\text{Ni}(\mu\text{-Cl})(\text{IPr})_2$ with 2,6-lutidine•HCl. In a glovebox, $[\text{Ni}(\mu\text{-Cl})(\text{IPr})_2$ (0.030 g, 0.031 mmol) and 2,6-lutidine•HCl (0.0089 g, 0.062 mmol) were added to a round bottom flask equipped with a Teflon-coated magnetic stirbar. THF was added to the flask and the mixture was stirred for ~ 2 h. After removing volatile materials, the resulting solid and 1,4-dimethoxybenzene were dispersed in C_6D_6 and the yields of the products were determined by NMR.

X-ray diffraction studies. Experiments were performed on single crystals of **1** and **2**. The single crystals of **1** and **2** were grown at $-40\text{ }^{\circ}\text{C}$ from toluene/hexanes. The crystals were removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. Crystals were affixed to a glass fiber or a cryoloop using the oil, frozen in a nitrogen stream, and optically centered. Graphite monochromators were employed for wavelength

selection of the Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS)⁴ and refined against F^2 on all data by full matrix least squares with SHELXL-97.⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model.

Computational Methods. All calculations were performed using the Gaussian03 (G03) program package,⁶ with the Becke three-parameter hybrid exchange and the Lee–Yang–Parr correlation functionals (B3LYP).^{7–9} The 6–31G* basis set was used for H, C and N,¹⁰ along with LANL2DZ energy-consistent pseudopotentials for Ni.^{11,12} All geometry optimizations were performed in C₁ symmetry with subsequent vibrational frequency analysis to confirm that each stationary point was a minimum on the potential energy surface. The percentage of Ni or halide character in the occupied (canonical) molecular orbitals (MOs) and virtual orbitals were calculated from a full population analysis using eq. (1),

$$\% \text{ Orbital Character}_{(\text{Ni,Cl})} = \frac{\sum \phi_{(\text{Ni,Cl})}^2}{\sum \phi_{(\text{all})}^2} \times 100\% \quad (1)$$

where $\sum \phi_i$ ($i = \text{Ni, Cl or all}$) is the sum of the squares of the eigenvalues associated with the atomic orbital (AO) of interest and all of the AOs in a particular MO, respectively. The vertical singlet transition energies of the complexes were computed at the time-dependent density functional theory (TD-DFT) level within G03 using the ground state optimized structure.

4 Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

5 Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997

6 Frisch, M. J. et al. Gaussian 03, revision C.02; Gaussian: Wallingford, CT, 2004.

7 Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

8 Becke, A. D. *Phys. Rev. A: Gen. Phys.* **1988**, *38*, 3098-3100.

9 Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785-789.

10 Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986.

11 Wedig, U.; Dolg, M.; Stoll, H. *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Springer: Dordrecht, The Netherlands, 1986.

12 Andrea, D.; Haeussermann, U.; Dolg, M.; Stoll, H. Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123-141.

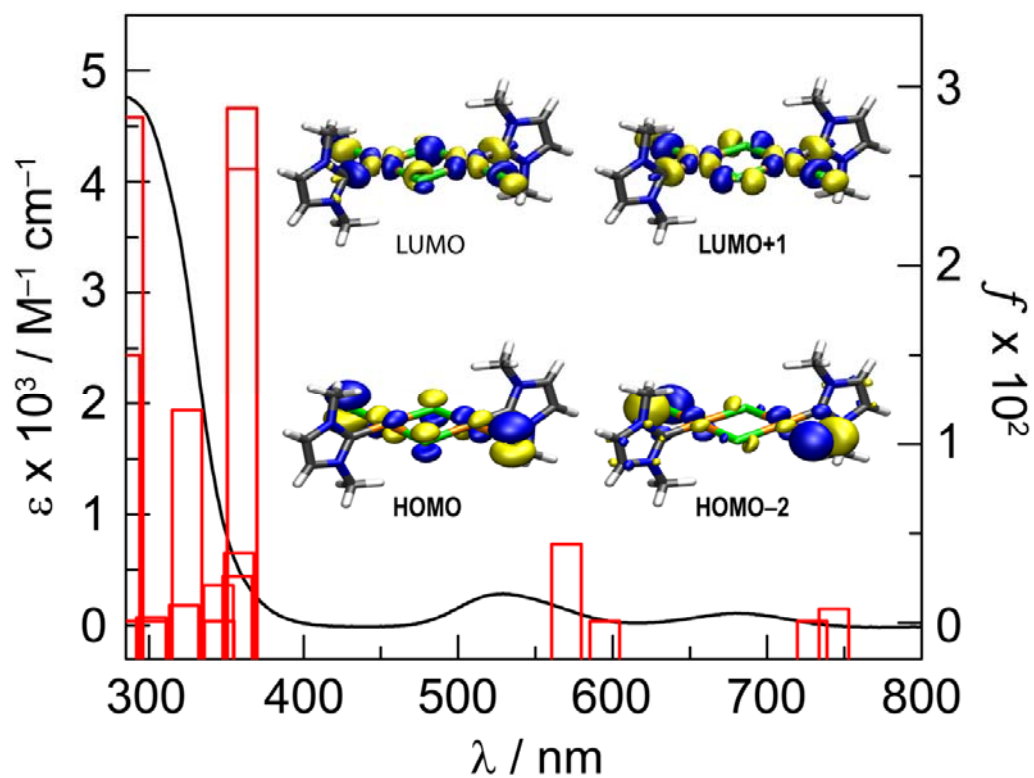


Figure S1. UV-vis spectrum of **1** (—) in toluene, calculated transitions (red bars) of **1-S**, and selected molecular orbitals involved in calculated transitions.

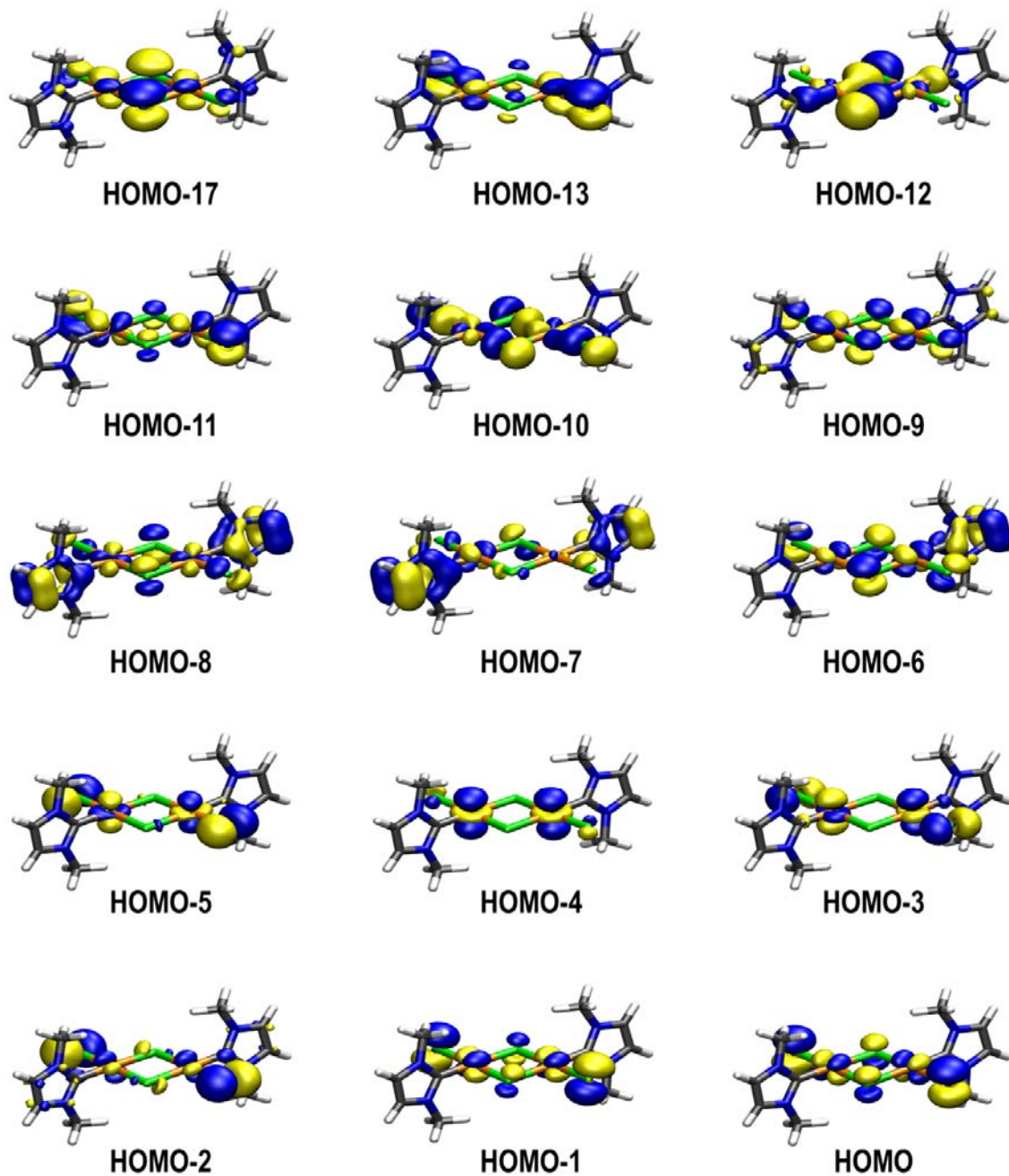


Figure S2. The list of occupied orbitals involved in calculated transitions between 360.39–301.40 nm.

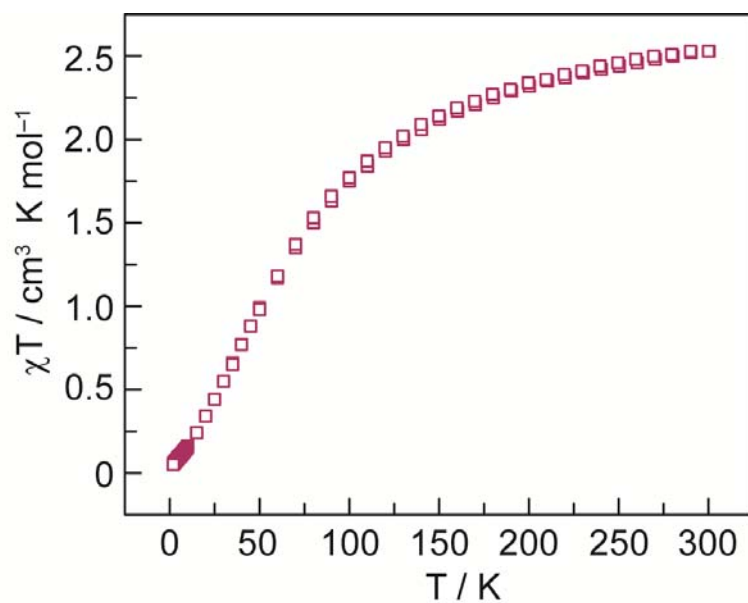


Figure S3. SQUID magnetometry (at 5000 Oe) of **1-T** with tetrahedral geometry, which was recrystallized from toluene/hexanes. ($\chi T_{\text{at } 300 \text{ K}}$ of **1-T**: $2.53 \text{ cm}^3 \text{ K mol}^{-1}$ and $\chi T_{\text{at } 295 \text{ K}}$ of toluene solution of **1** measured by Evans method: $2.30 \text{ cm}^3 \text{ K mol}^{-1}$; the ratio of **1-T** in solution estimated by the ratio of these values is ca. 90%).

Table S1. Crystal Data and Structure Refinement for **1**

Identification code	10019	
Empirical formula	C ₅₄ H ₇₂ N ₄ Cl ₄ Ni ₂	
Formula weight	1036.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P2(1)/n</i>	
Unit cell dimensions	<i>a</i> = 12.4363(8) Å	$\alpha = 90^\circ$
	<i>b</i> = 13.7770(8) Å	$\beta = 94.5330(10)^\circ$
	<i>c</i> = 16.4633(10) Å	$\gamma = 90^\circ$
Volume	2811.9(3) Å ³	
<i>Z</i>	2	
Density (calculated)	1.224	
Absorption coefficient	0.896	
F(000)	1096	
Crystal size	0.20 × 0.15 × 0.10 mm ³	
θ range for data collection	1.93 to 29.13°	
Index ranges	$-15 \leq h \leq 17, -18 \leq k \leq 18, -22 \leq l \leq 22$	
Reflections collected	59460	
Independent reflections	7557 [<i>R</i> _{int} = 0.0260]	
Completeness to $\theta = 27.48^\circ$	99.9%	
Absorption correction	SADABS	
Max. and min. transmission	0.8411, 0.9157	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	7557 / 0 / 297	
Goodness-of-fit on <i>F</i> ²	1.017	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0242, <i>wR</i> ₂ = 0.0605	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0284, <i>wR</i> ₂ = 0.0631	
Largest diff. peak and hole	0.393 and -0.234 e/Å ⁻³	

^a GOF = $(\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined. ^b *R*₁ = $\sum ||F_o - |F_c|| / \sum |F_o|$. ^c *wR*₂ = $(\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$.

Table S2. Crystal Data and Structure Refinement for **2**

Identification code	10230	
Empirical formula	C ₃₄ H ₄₅ N ₃ Cl ₂ Ni	
Formula weight	625.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 34.143(4)$ Å	$\alpha = 90^\circ$
	$b = 15.1633(19)$ Å	$\beta = 106.720(2)^\circ$
	$c = 12.8525(17)$ Å	$\gamma = 90^\circ$
Volume	6372.7(14) Å ³	
Z	8	
Density (calculated)	1.304	
Absorption coefficient	0.804	
F(000)	2656	
Crystal size	0.45 × 0.20 × 0.10 mm ³	
θ range for data collection	1.25 to 25.35°	
Index ranges	$-41 \leq h \leq 41, -18 \leq k \leq 18, -15 \leq \ell \leq 15$	
Reflections collected	52647	
Independent reflections	5835 [$R_{\text{int}} = 0.0696$]	
Completeness to $\theta = 28.29^\circ$	100.0 %	
Absorption correction	SADABS	
Max. and min. transmission	0.7137, 0.9239	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5835 / 0 / 371	
Goodness-of-fit on F^2	1.032	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0316, wR_2 = 0.0686$	
R indices (all data)	$R_1 = 0.0480, wR_2 = 0.0766$	
Largest diff. peak and hole	0.347 and -0.279 e/Å ⁻³	

^a GOF = $(\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

^b $R_1 = \sum |F_o - |F_c|| / \sum |F_o|$. ^c $wR_2 = (\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$.

Table S3. Cartesian coordinates of calculated optimized geometry for **1–S**

Atom Type	Coordinates (Angstroms)		
	x	y	z
Ni	1.556786	-0.563174	0.225436
Ni	-1.555377	0.544362	-0.267427
Cl	2.529362	-2.360988	1.063840
Cl	-2.531347	2.386750	-0.998314
Cl	-0.608919	-1.378876	0.503555
Cl	0.610255	1.321673	-0.636298
C	3.279242	0.155663	-0.021021
C	-3.278666	-0.149320	0.037207
N	3.892449	1.078521	0.753876
N	-3.950232	-1.025503	-0.743139
N	4.158032	-0.141765	-1.004101
N	-4.100969	0.125222	1.074261
C	5.161729	1.354007	0.264806
C	-5.200680	-1.293493	-0.203701
H	5.820807	2.060919	0.743841
H	-5.897968	-1.966939	-0.676766
C	5.326546	0.588715	-0.844807
C	-5.292987	-0.572149	0.943111
H	6.154232	0.504003	-1.531294
H	-6.084068	-0.498719	1.672732
C	-3.763716	1.038350	2.163938
H	-3.035511	0.574736	2.835185
H	-3.347125	1.952759	1.737197
H	-4.674275	1.272904	2.718930
C	-3.449758	-1.544929	-2.013155
H	-3.646207	-0.831849	-2.818927
H	-2.375433	-1.712750	-1.926213
H	-3.947079	-2.493130	-2.228651
C	3.896574	-1.107398	-2.069177
H	3.456568	-2.002909	-1.626429
H	3.212463	-0.681659	-2.808583
H	4.842718	-1.362306	-2.550890
C	3.317778	1.637979	1.974630
H	2.254447	1.820804	1.813565
H	3.449551	0.942591	2.808509
H	3.817133	2.582931	2.198986