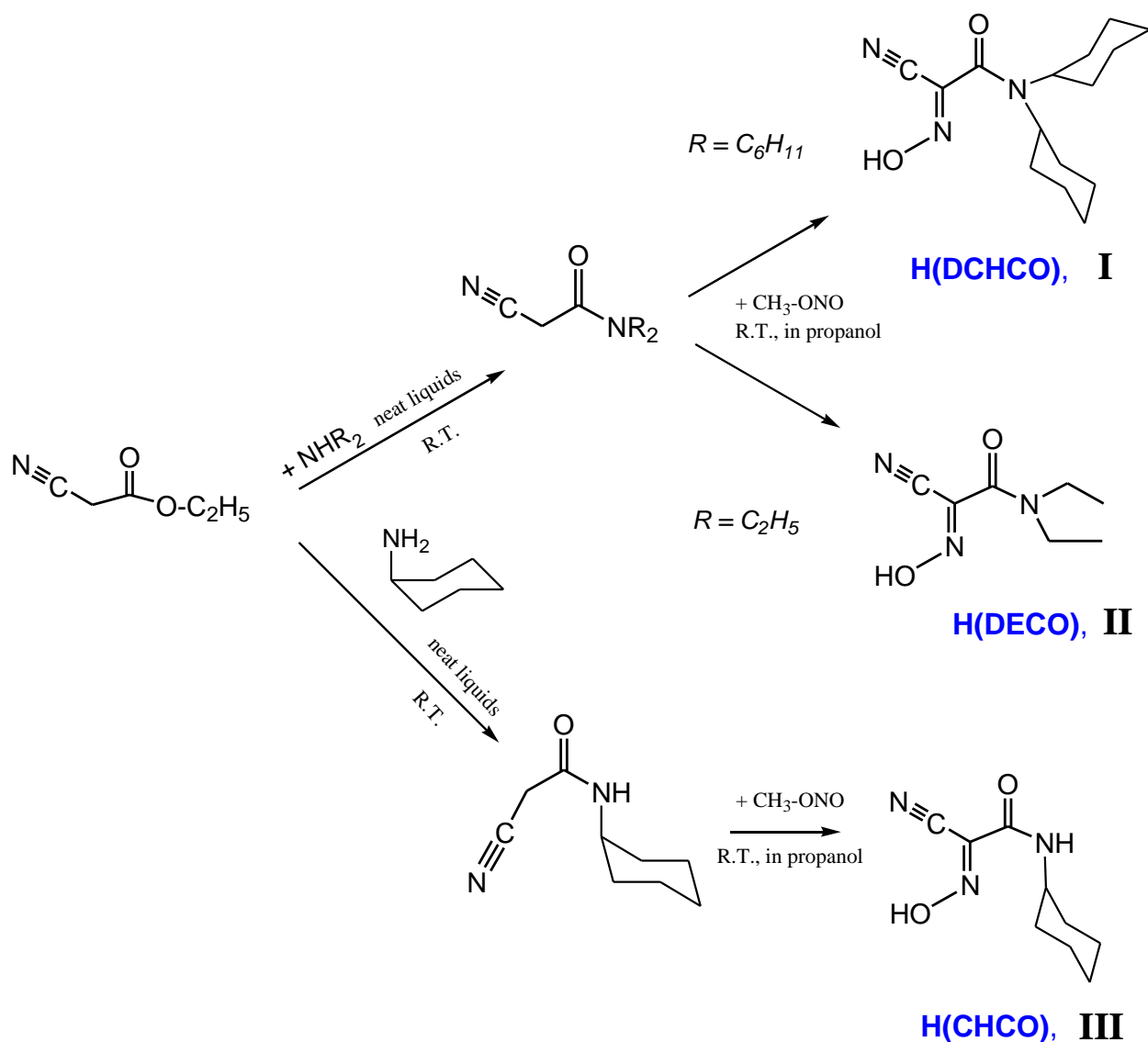


**Matthew Keene, 2008-2009**

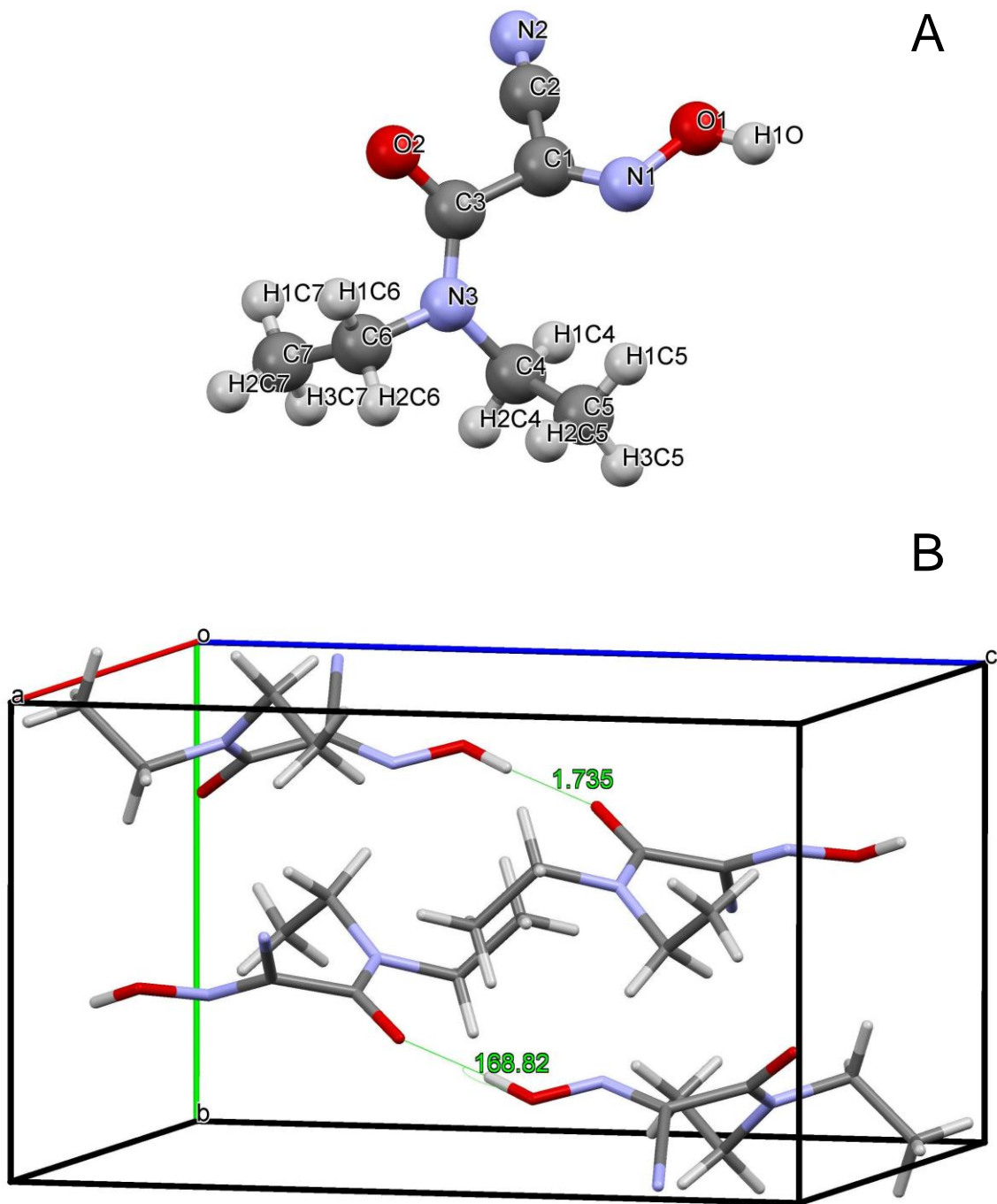
Matthew was enrolled in Undergraduate Research classes CHM 399 and CHM 499 and during these two semesters worked in my research laboratory. His project was dedicated to the *preparation of new amide-based cyanoxime ligands*.

The method was using commercially available neat ethyl-cyanoacetate as precursor and react it with neat secondary and primary amines as explained in Figure 1. The amidation reaction Matt normally carried out at room temperature to avoid cleavage of the newly-formed amide bond and formation of cyanoacetic acid ammonium salts as we observed in abundance in the past. Thus, solid amides were filtered off, washed with a few milliliters of alcohol, then dry benzene, and then dried under vacuum. Matthew professed this reaction very well and supplied my research laboratory with batches of a variety of amides in substantial quantities. These amides were transformed into oximes using two major routes: 1) nitrosation reaction using  $\text{NaNO}_2$  and acetic acid carried at  $0^\circ\text{C}$ , 2) nitrosation reaction at basic conditions using methyl nitrite  $\text{CH}_3\text{-ONO}$  gas. The second method was always used when the first reaction did not lead to the target oxime. The main reason for that failure was, as we dissected in the group, was insufficient reactivity of the methylene group of substituted acetonitrile  $\text{NC-CH}_2\text{-C(O)NR}_2$  towards nitrosating agent. Thus, Matthew prepared three new cyanoximes: 2-oximino-2-cyano-N,N'-diethylacetamide (we abbreviated it as **H(DECO)**), 2-oximino-2-cyano-N-cycloheptylacetamide (was abbreviated as **H(CHCO)**) and 2-oximino-2-cyano-N,N'-dicyclohexylacetamide (abbreviated as **H(DCCO)**).



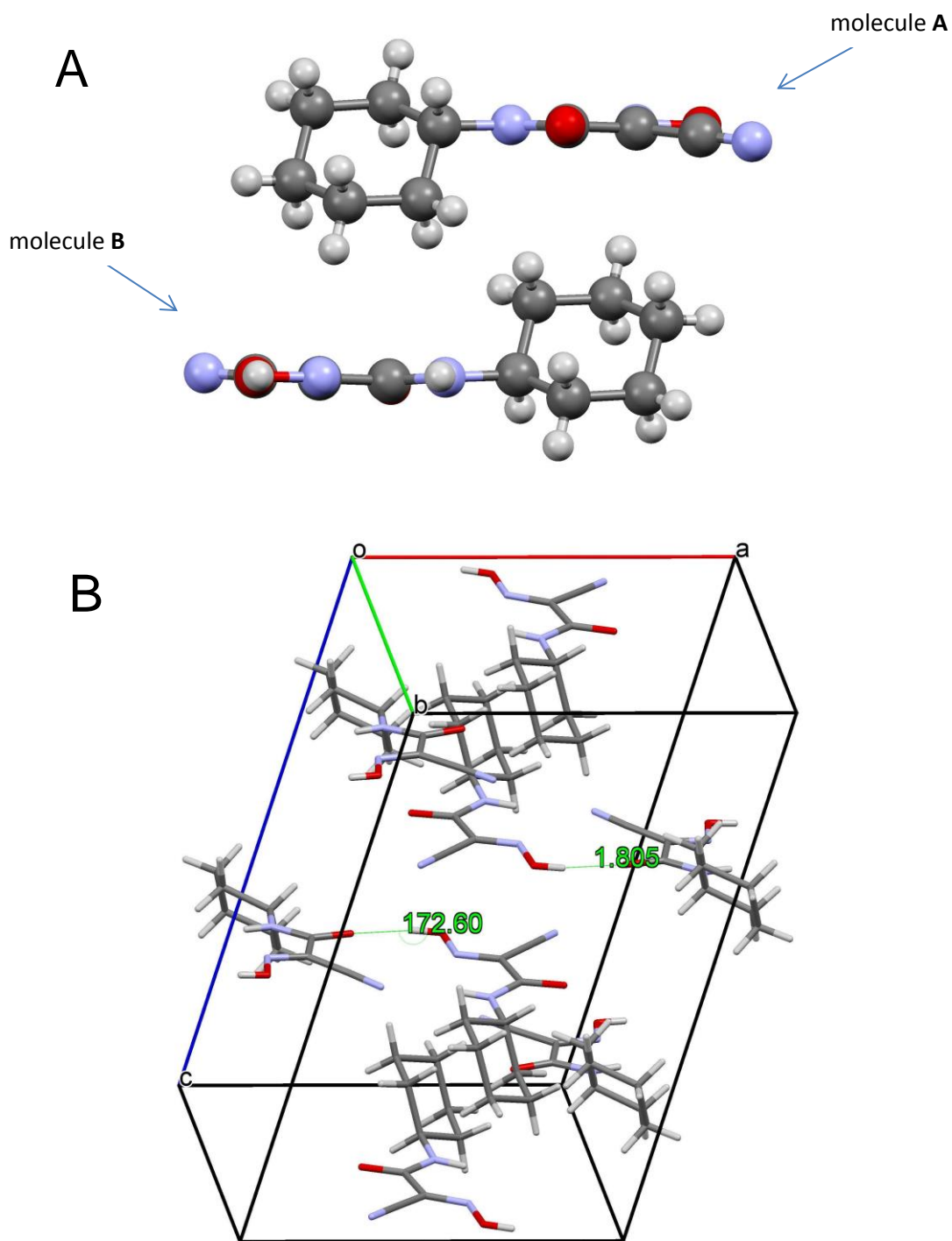
**Figure 1. Developed synthetic routes to new amide-containing cyanoximes ligand for inorganic chemistry.**

Matthew grew crystals of these three new cyanoximes and their structures were determined. Representative figures are located in Figure 2-4. These ligands behave in a similar fashion as all other previously obtained cyanoximes: they change color to yellow in basic media, because of the deprotonation, forming conjugated in the cyanoxime core anions  $[\text{NC}-\text{C}(\text{NO})-\text{C}(\text{O})\text{NR}_2]^-$ . The color originates from low intensity ( $\epsilon \sim 60$ )  $n-\pi^*$  transition around 400 nm.



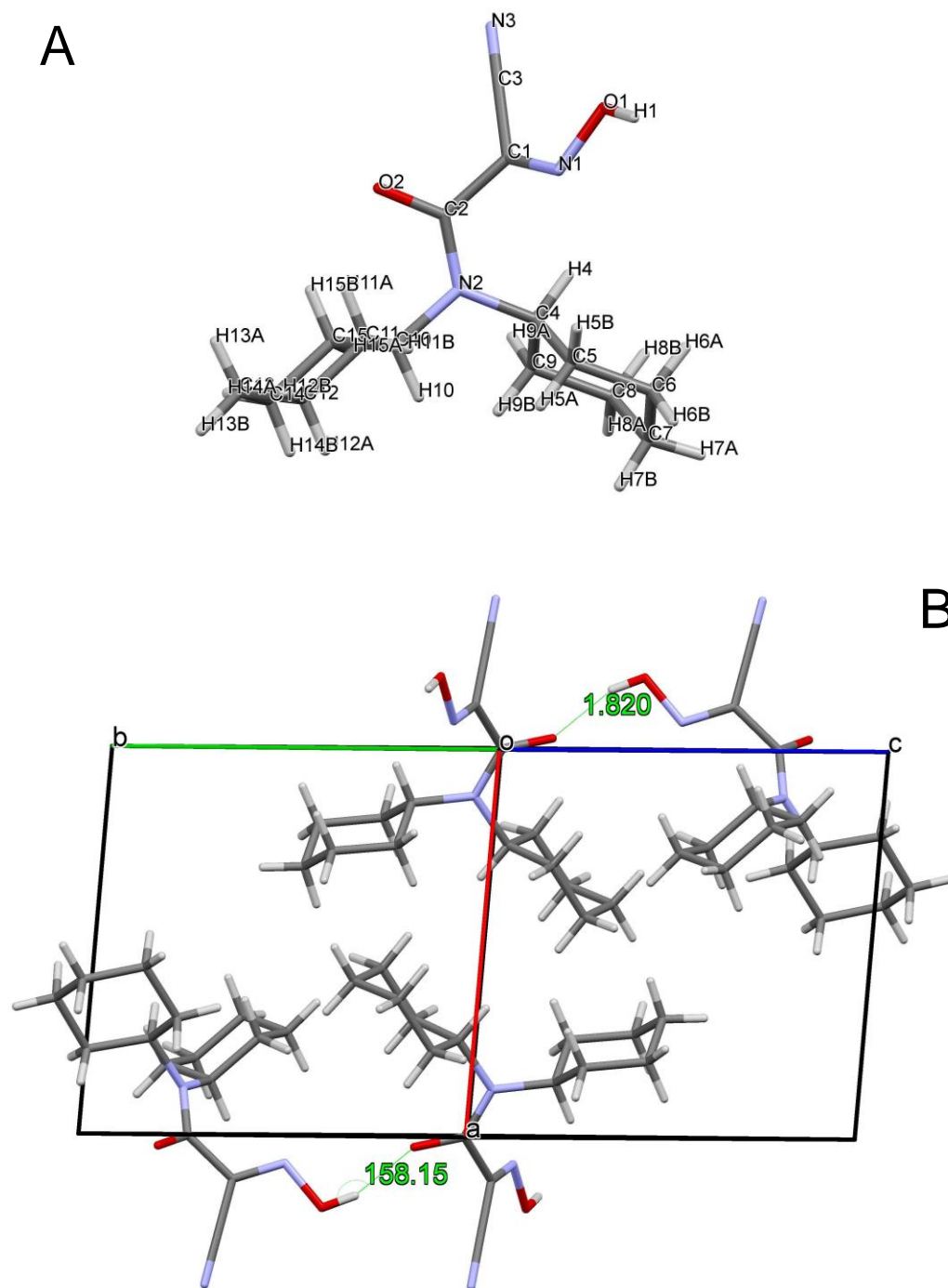
**Figure 2.** Molecular structure and numbering scheme for H(DECO), II (A), and prospective view of the unit cell content (B) showing H-bonding in the structure and its geometry.

**Crystal data:** T=153 K; in P2<sub>1</sub>/c; R1 = 4.7%; GOF = 1.038.



**Figure 3.** Molecular structure and numbering scheme for H(CHCO), III, with two independent molecules in the ASU indicated by arrows (A), and prospective view of the unit cell content (B) showing H-bonding in the structure and its geometry.

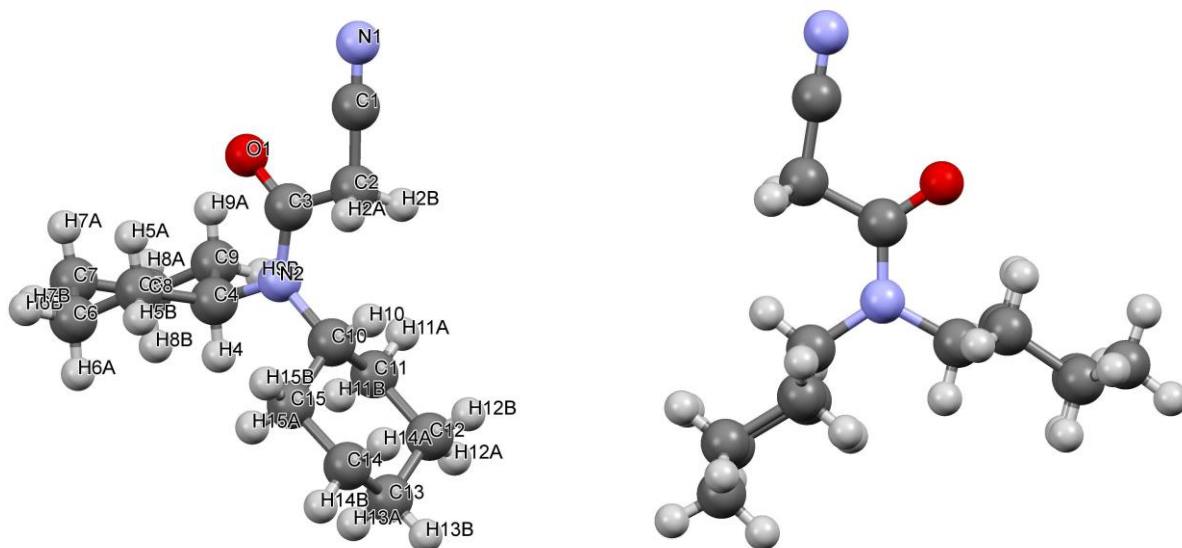
**Crystal data:** T=150 K; in P2<sub>1</sub>/n; R1 = 4.18%; GOF = 1.030.



**Figure 4.** Molecular structure and numbering scheme for H(DCHCO), I, (A), and prospective view of the unit cell content along [110] (B) showing H-bonding in the structure and its geometry.

**Crystal data:** T=296 K; in P2<sub>1</sub>/c; R1 = 3.85%; GOF = 1.027.

Also, Matthew obtained suitable for the X-ray analysis crystals of one of the precursors – an acetonitrile initial for the cyanoxime **I**. Its crystal structure is presented below in Figure 5. This compound crystallizes in non-centrosymmetric space group  $Pna2_1$ . It is rather interesting finding in light of search for organic compounds that exhibit non-linear-effect (NLO), which makes this substituted acetonitrile quite appropriate for studies of the second harmonic generation effect (SHG).



**Figure 5.** Molecular structure and numbering scheme for the substituted acetonitrile – precursor for **I**, (A), and a side view showing an adoption of conformation by two cyclohexyl rings (B).

**Crystal data: T=296 K; in  $Pna2_1$ ; R1 = 4.4%; GOF = 0.991.**

As it is seen from presented material Matthew Keene was very successful and productive investigator in my research group. I offered Matthew to stay in the group and earn his MS degree working on a continuation of the project to which he had a very good foundation. Unfortunately, he declined my offer and went to his native St. Louis and got accepted for Ph.D. program at the University of Missouri – St.Louis (UMSL). Sadly, he later dropped out of the program...

**One major peer-reviewed paper was published with Matthew Keene:**

Klaus, D.R., Keene, M., Silchenko, S., Berezin, M., Gerasimchuk, N. "1D Polymeric Platinum Cyanoximate: A Strategy toward Luminescence in the Near-Infrared Region beyond 1000 nm." *Inorganic Chemistry*, **2015**, 54 (4), 1890-1900.

Most likely there will be two more papers written on results based on Matthew work when the whole data and relevant chemistry will be completed.

**Conference presentation with Matthew:**

*48<sup>th</sup> Midwest Regional ACS Meeting (October 16-19, 2013; Springfield, MO)*

D. R. Klaus,\* M. Keene,\* N. Gerasimchuk. "Synthesis, Spectra, and Crystal Structures of N,N' diethylamide-2-cyano-2-oximino-acetamide and its Pt<sup>+2</sup> and Pd<sup>+2</sup> cyanoximates." Abstracts, 48<sup>th</sup> Midwest Regional ACS Meeting, Springfield, MO. United States, October 16-19; MWRM-9.