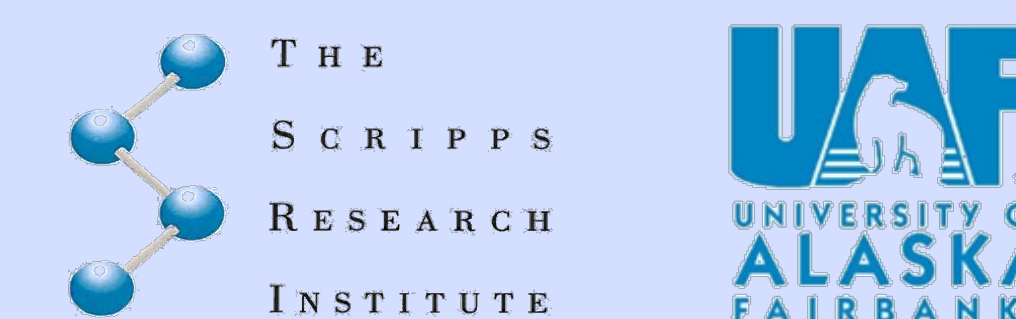


Preparation of a Novel Frequency Doubling Coordination Complex

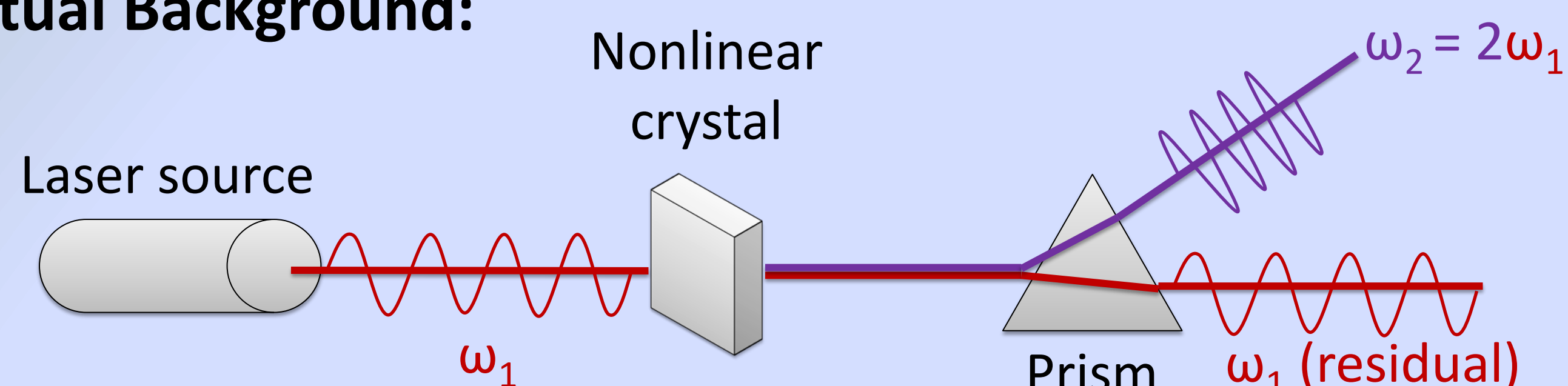
by Julia Duncan

Department of Chemistry and Biochemistry, University of Alaska Fairbanks



Abstract: The goal of this project was to synthesize an organic ligand that can be used to make a coordination complex with the appropriate structural features to produce frequency doubled light. Partial synthesis of the ligand was accomplished as confirmed by proton nuclear magnetic resonance (^1H NMR) spectroscopy and electrospray mass spectrometry. Additional steps remain to be explored and completed, yet it is expected that the chiral nature of the target ligand will fulfill the structural criteria necessary for frequency doubling in the crystalline phase.

Conceptual Background:



High intensity light passes through a crystalline medium and light of twice the frequency is produced. Output intensity is described by hyperpolarizability, β .

Main criteria are structurally dependent:

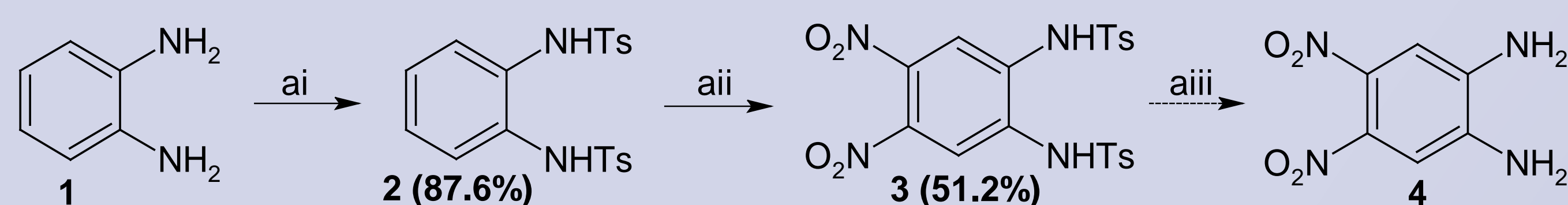
- Must be non-centrosymmetric, have a low-energy charge transfer transition, and produce high dipolar oscillation when exposed to ω .
- Features: $[\text{e}^- \text{ donor}] - [\pi \text{ bridge}] - [\text{e}^- \text{ acceptor}]$
- Target: $[\text{Cu}(\text{I})] - [\pi \text{ bridge}] - [\text{dinitro}]$
- Cuprous ions ($\text{Cu}(\text{I})$) donate d-electrons to the π scaffolding of the ligand while dinitroquinoxaline groups act as electron acceptors.

$$\beta \propto \frac{\mu_{ge}^2 (\mu_{ee} - \mu_{gg})}{E_{ge}^2}$$

Can be used in fiber optic cables, biological dyes, or optical information technology.

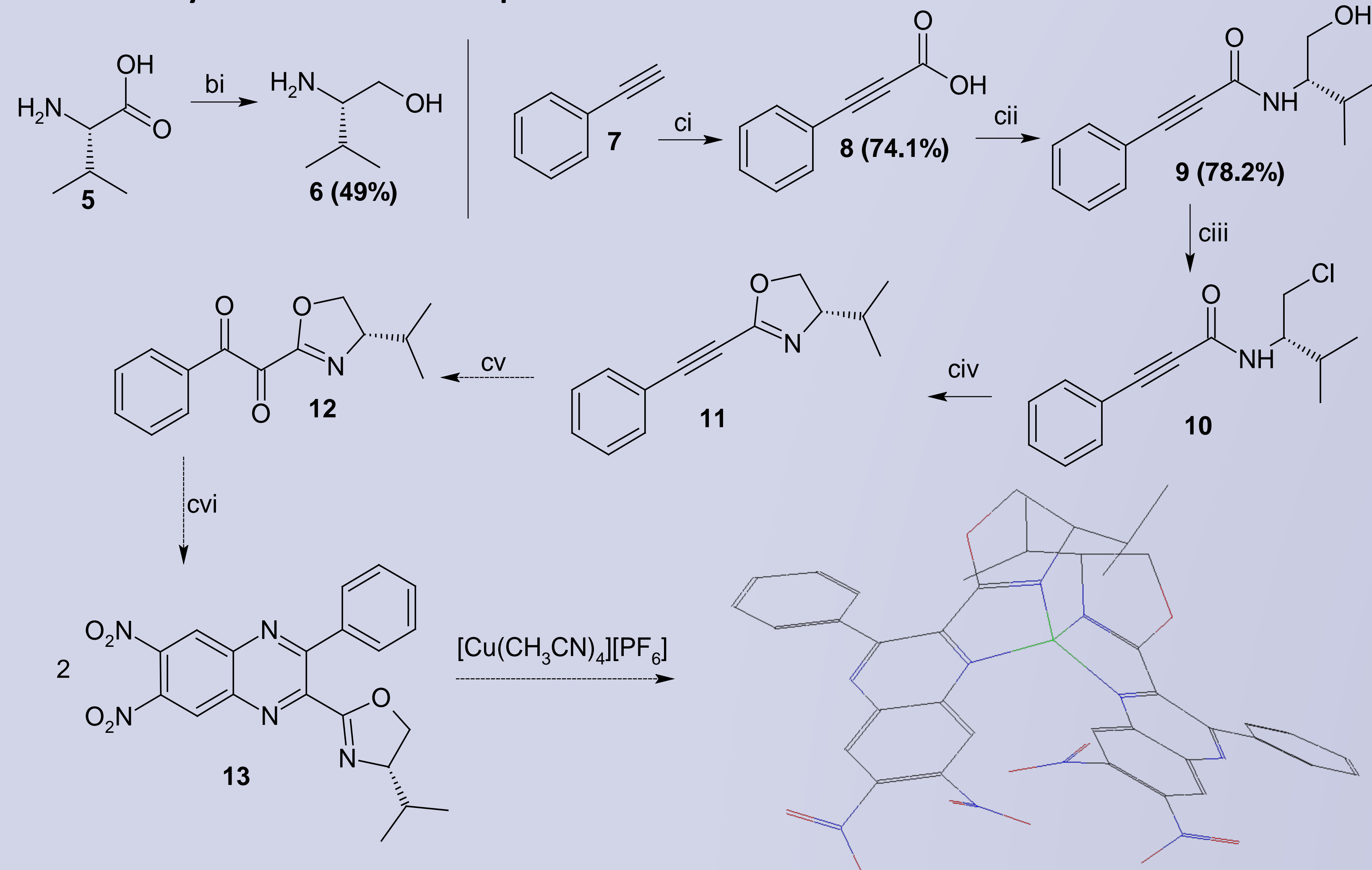
Method of Synthesis:

Scheme 1: Synthesis of 4,5-dinitrobenzene-1,2-diamine



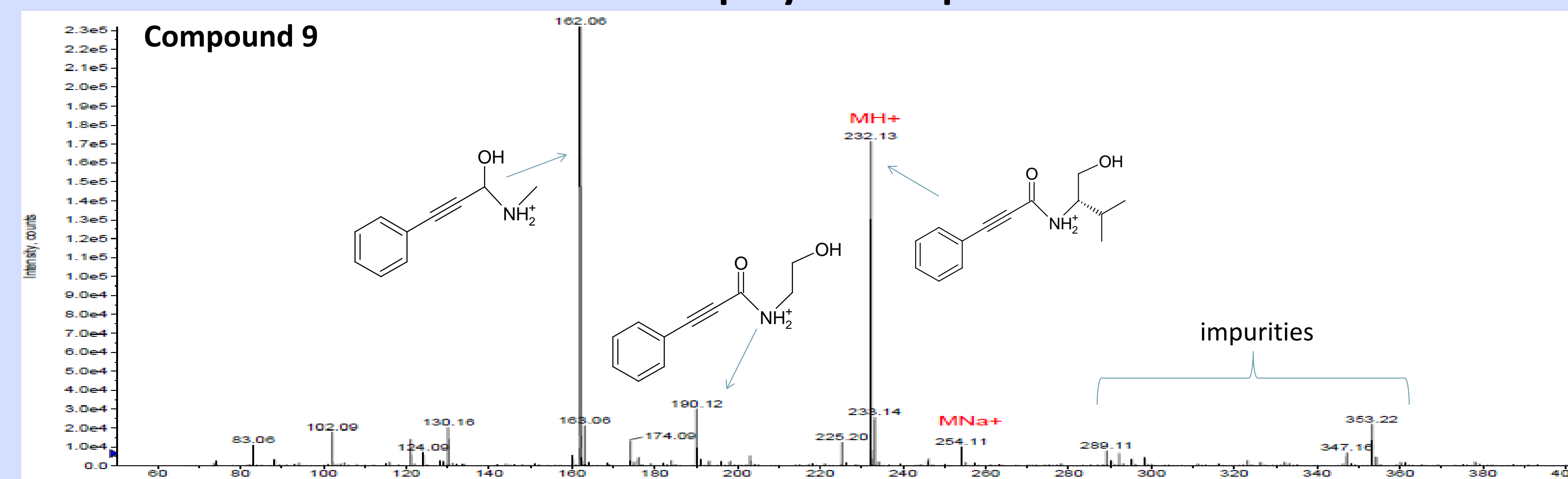
ai) 2TsCl, 2Py, CH_2Cl_2 ; H_2O [1] aii) HNO_3 (fuming), glacial AcOH, heat [2] aiii) H_2SO_4 , H_2O , heat [2]

Scheme 2: Synthesis of Chiral Complex

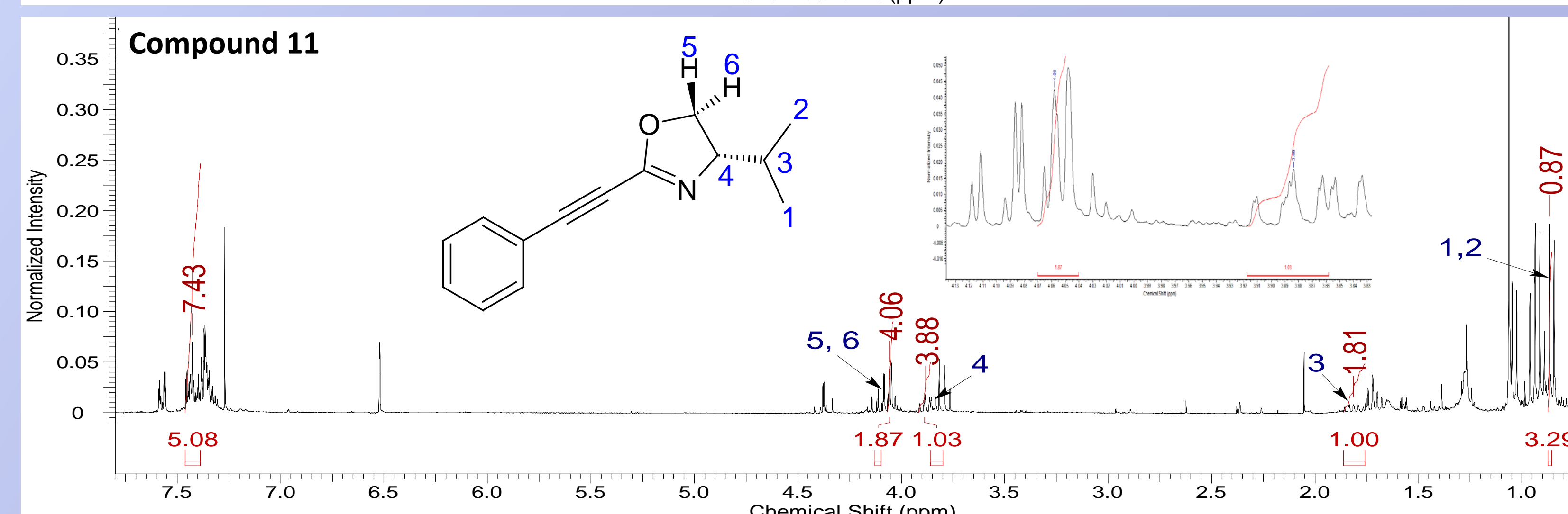
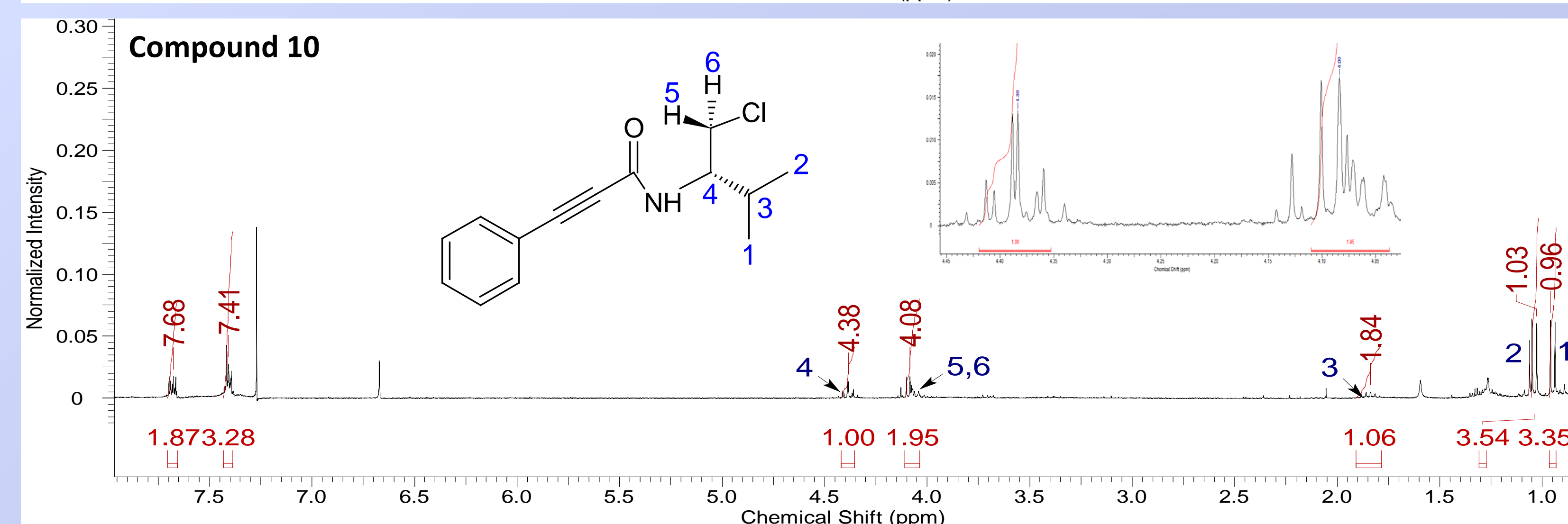
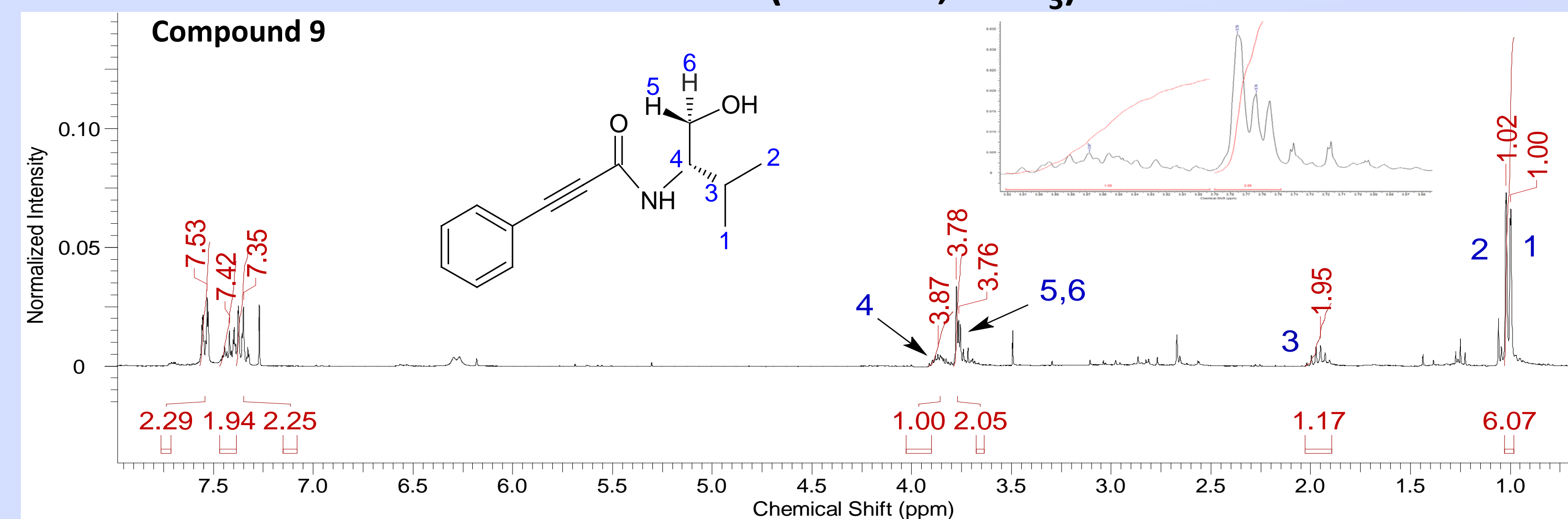


bi) NaBH_4 , I_2 , THF, 0°C ; D; MeOH, 0°C ; KOH [3] ci) $n\text{BuLi}$, THF, CO_2 , -50°C [4] cii) NHS, DCC, **6**, rt [5] ciii) Et_3N , SOCl_2 , CH_2Cl_2 civ) THF, DBU, Δ cv) KMnO_4 , H_2O , Acetone [6] cvi) EtOH, **4**, Δ

Electrospray Mass Spectrum



^1H NMR (300MHz, CDCl_3)



Conclusion: Completion of the synthetic procedure remains to be done. However several difficult steps toward the target complex were elucidated, particularly compound 9 which involved peptide coupling with L-valinol. The result of this project contributed to a larger body of research involving synthesis of interesting frequency doubling coordination complexes.

- References:** [1] Paquette, L.A.; *et al. J. Org. Chem.*, **2009**, 74 (7), 2897
 [2] Cheeseman, G. W.H. *J. Chem. Soc.*, **1962**, 1170
 [3] McKennon, M.J.; Meyers, A.I. *J. Org. Chem.*, **1993**, 58, 3568-3571
 [4] Sai, H.; Ogiku, T.; Ohtani, A.. *Chem. Pharm. Bull.* **54** (12), 1686-1693
 [5] Cevallos, A; *et al. Tetrahedron: Asymmetry*, **2000**, 11 (21), 4407-4416
 [6] Chen, K.; *et al. Macromolecules*, **2005**, 38 (21), 8617-8624

Acknowledgments: Great thanks is due to Dr. F. Heitzler for his outstanding mentorship and guidance on all stages of this project. Thanks to Dr. C. Murphy for NMR instrument assistance and Dr. B. Edmonds for constructive input. Thanks to URSA for funding and the Scripps Research Institute for providing mass spectra.

