Synthesis and Binding Abilities of Bis(quinoxalino) Ligands

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Abstract

The need for environmentally safe practices has skyrocketed within the past few years, as soil and water are subject to transition metal accumulation. One way to deal with these contaminations is by use of peraza-crown macrocycles as ligands to remove these metals. Our project focuses on a unique synthesis of the peraza-crown macrocycle that avoids the common use of a metal skeleton. Through the use of the quinoxaline subunit, we are able to greatly increase the binding properties of the peraza-crown macrocycle and the rigidity of the overall molecule.

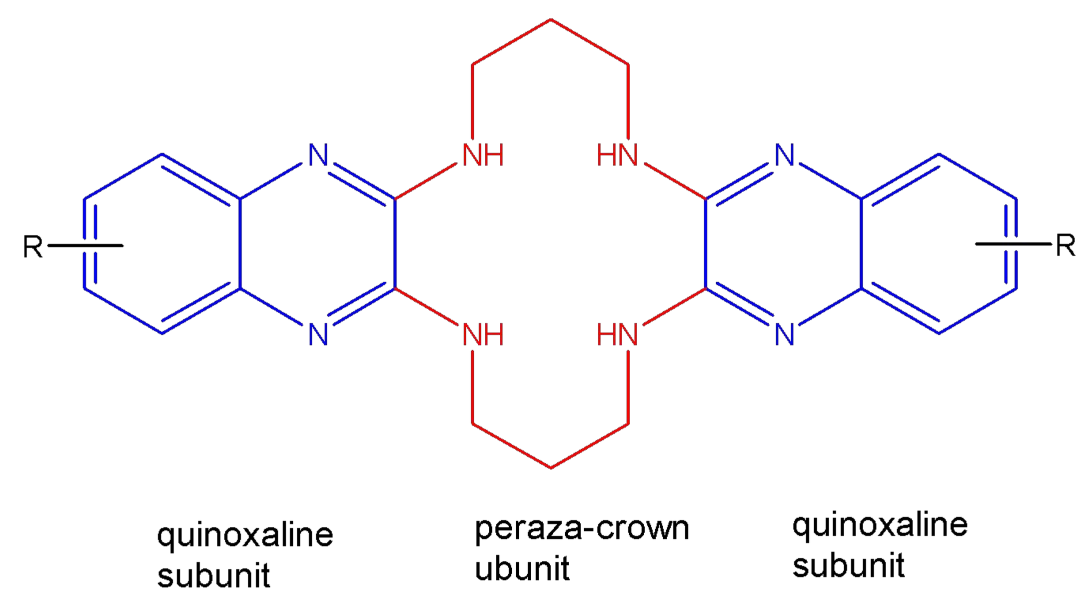

Figure 1

Introduction

Quinoxalines belong to a family of heterocycles in which two nitrogen atoms replace two carbon atoms in a naphthalene ring. Quinoaxlines have a large presence in biologically active compounds and processes. Applications of the moiety range from medicinal to agricultural. Nitrogen containing macrocyclic ligands, specifically peraza-crowns, robustly complex with transition metal cations. The rigidity of a macrocycle intensifies when subunits such as quinoxaline are integrated into the structure. This modifies the stability and selectivity of a metal-ligand interaction. By combining the rigidity of the quinoxaline and the good binding properties of the aza-crown macrocycle, we hypothesize that we can obtain beneficial compounds with biologically friendly properties.

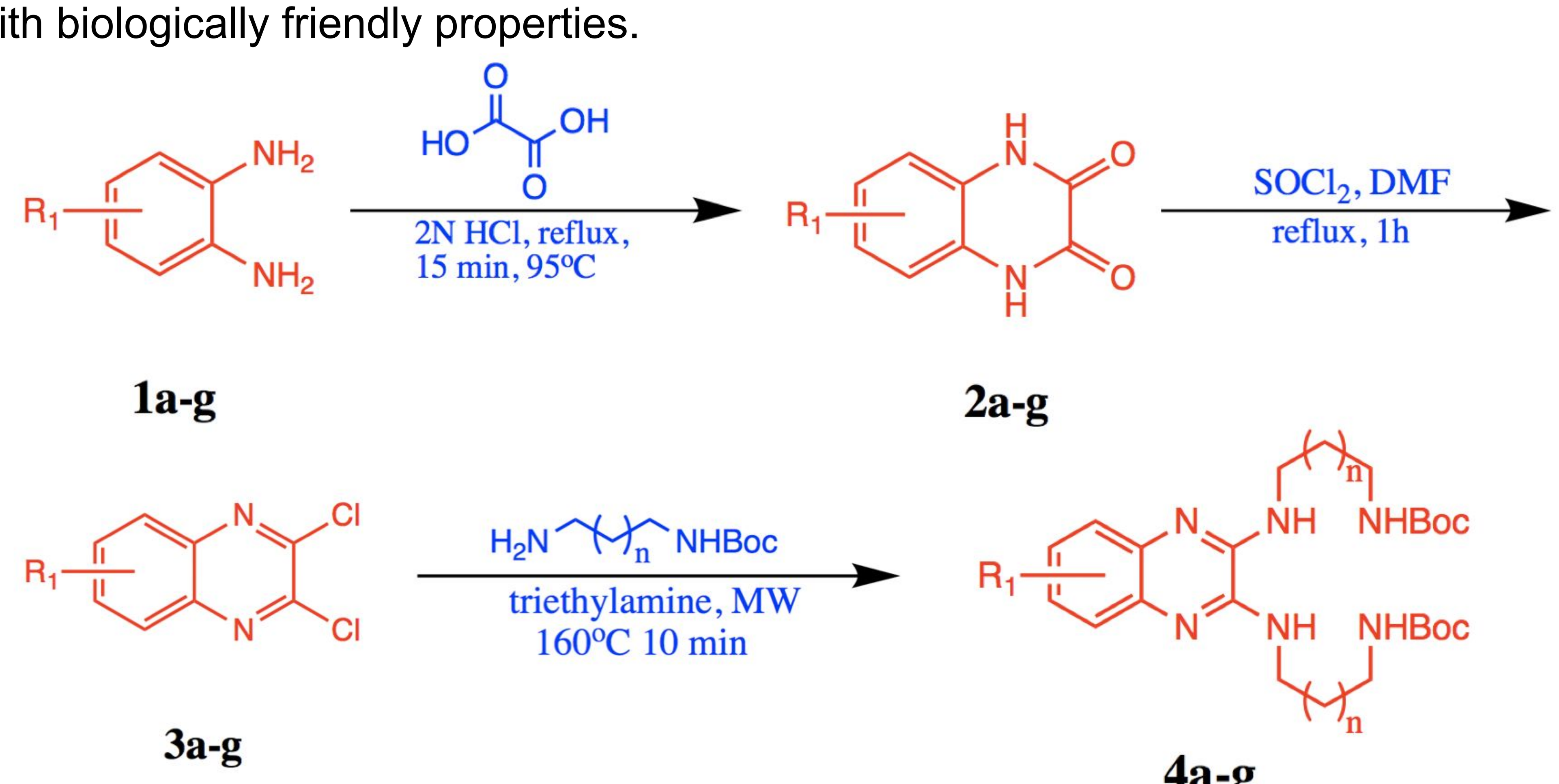

Figure 2

Results and Discussion

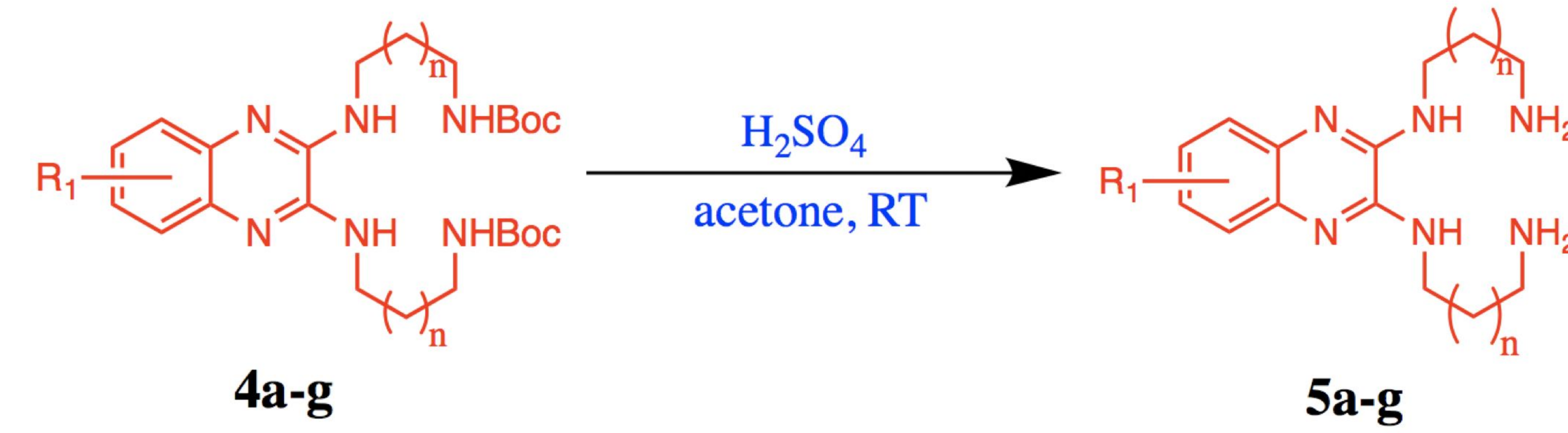

Figure 3

Oxalic acid in water was heated to 95°C, HCl and **1** were added. The temperature was maintained for 4 hours to give **2**. The compound **2** was refluxed in $SOCl_2$ and DMF for 3 hours. **3** was obtained after workup. To obtain **4**, the Boc-protected diamine was dissolved in trimethylamine. Then **3** was added and the mixture was microwaved for 5 minutes at 160°C. One more period of 5 minutes of microwaving followed with the addition of more protected amine. Then, compound **4** was dissolved in acetone and deprotected with H_2SO_4 to give product **5**. Product **6** was achieved through microwaving **5** with **3** at 160°C for an hour. The NMR shows product present, but yield was very low.

Summary and Future Work

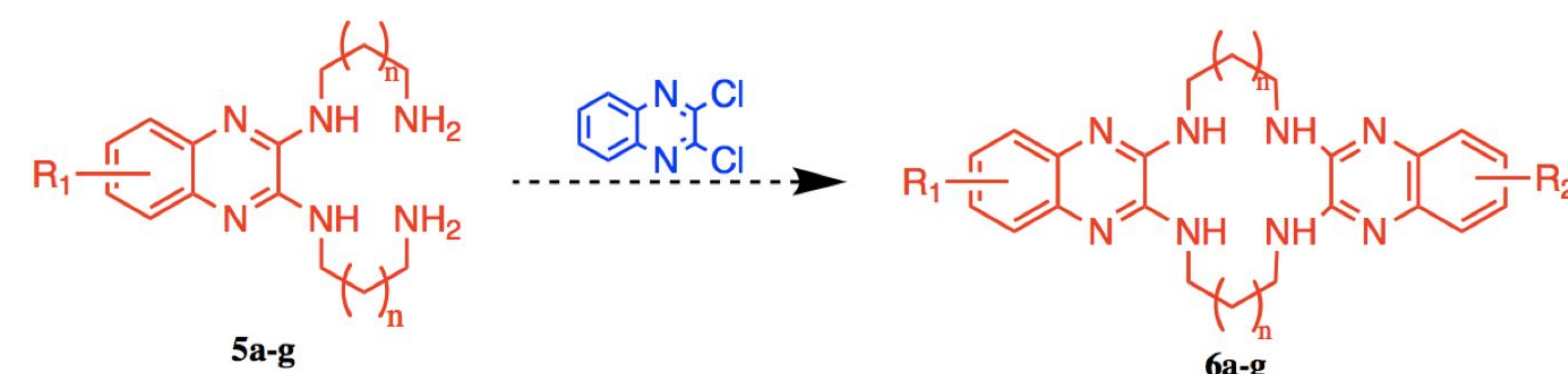

Figure 4

Entry	R_1	R_2	n	Yield (5)	Yield (6)
a	H	H	0	99%	13%
b	4,5-dimethyl	4,5-dimethyl	0	99%	-
c	H	H	1	99%	13%

For our continued work, we will follow the synthesis as outlined in Figure 4 and work to increase yield of **6**. Synthesis of the compound **6** will be binding **3** to **5**. Different peraza-crown macrocycles can be similarly synthesized by lengthening the diamine and by changing the R-groups. The final peraza-crown molecule will be tested for metal ion binding properties. These ligands will be introduced into reaction mixtures containing common metal catalysts such as Cu and Pd. The purpose of this is to determine the geometrical binding and the overall efficacy of using these ligands as agents that can selectively remove transition metals.