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Towards the Design and Syntheses of Novel Triads Comprising Single Robson-Type
Macrocyclic Dicopper(II) Cores Flanked by Two Terminal Polypyridyl Ruthenium(II)
Complexes

A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

by

L. Shane Moody

December 2008

Jeffrey G. Wardeska, Ph.D., Chair

Chu-Ngi Ho, Ph.D.

Scott J. Kirkby, Ph.D.

Keywords: Cross-Coupling

ABSTRACT

Towards the Design and Syntheses of Novel Triads Comprising Single Robson-Type Macrocyclic Dicopper(II) Cores Flanked by Two Terminal Polypyridyl Ruthenium(II) Complexes

by

L. Shane Moody

Progress toward the syntheses of new tetranuclear bimetallic complexes of copper(II) and ruthenium(II) was realized. The designed triads comprise a central binuclear copper(II) complex with a tetraaminodiphenolate macrocyclic Robson-type compartmental ligand. In the envisioned complexes, the macrocyclic core is further functionalized by attachment of two polypyridyl ruthenium(II) complexes. A novel dibrominated dicopper(II) Robson complex was formed by the 2:2:2 condensation reaction of 4-bromo-2,6-diformylphenol and 1,3-diaminopropane with cupric chloride. Similarly, a new dibrominated dizinc(II) was synthesized from zinc tetrafluoroborate and the same diamine and dialdehyde. The new dicopper(II) complex did not heterocouple with borylated substrates under explored Suzuki reaction conditions. 5-Bromo-2-(methoxymethoxy)benzene-1,3-dicarboxaldehyde successfully heterocoupled with 4-*tert*-butylphenylboronic acid under Suzuki conditions. 4'-(4-Neopentylglycolatoboronphenyl)-2,2':6',2''-terpyridine also coupled with 5-bromo-2-(methoxymethoxy)benzene-1,3-dicarboxaldehyde to give, after deprotection, 2,6-diformyl-4-(4-[2,2':6',2''-terpyridin]-4'-ylphenyl)phenol. This new dialdehyde, a precursor to the title complexes, was treated with (4'-(4-methylphenyl)-2,2':6',2''-terpyridine)RuCl₃ under reducing conditions; however, the desired [(4'-(4-methylphenyl)-2,2':6',2''-terpyridine)Ru(4'-(3,5-diformyl-4-hydroxyphenyl)-2,2':6',2''-terpyridine)]²⁺ was neither isolated from nor detected in the reaction mixture.

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CHAPTER 1

INTRODUCTON

Supramolecular Chemistry Defined

Supramolecular chemistry is a vast and growing cross- and inter-disciplinary area of chemistry. In his Nobel lecture¹, 1987 laureate Jean-Marie Lehn defined supramolecular chemistry "...as 'chemistry beyond the molecule', bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces...". In their introductory textbook on the subject², Jonathan W. Steed and Jerry L. Atwood state that "...'chemistry beyond the molecule'...means that the chemist is at liberty to study pretty much any kind of interaction he or she pleases-except some covalent ones. The situation is rather reminiscent of the hubris of some inorganic chemists in jokingly defining that field as 'the chemistry of all of the elements except for some of that of carbon'...".

Generally, for a species to be considered supramolecular, the molecular components that make up the supermolecule must largely retain their individual properties, regardless of the mode of connection of those components. That is to say, the components *can* be covalently connected, as well as hydrogen-, datively-, or otherwise bonded, as long as localization of the intrinsic properties of the component molecules is not severely compromised. Should significant delocalization of properties occur, then the species is not considered supramolecular but can be best described merely as a large molecule. This distinction is illustrated graphically in Figure 1,³ where a complex chemical species, A~B, interacts with light or is subjected to redox processes. In this illustration, A and B are subunits of the dyad, and ~ is the bond (covalent or other type of

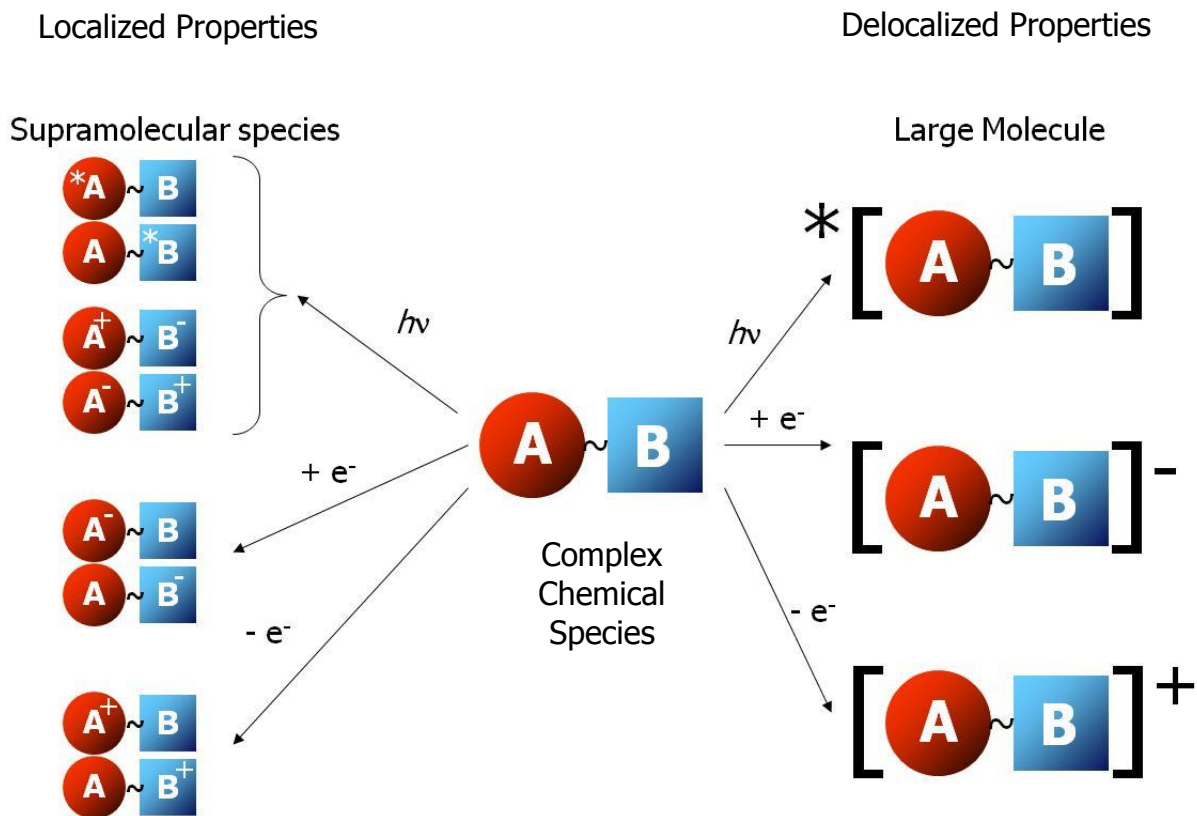


Figure 1. Schematic Representation of a Complex Chemical Species Illustrating Localization (Supramolecular Species) or Delocalization (Large Molecule) of Properties Upon Photo- or Electrochemical Input. Adapted from Balzani et al.³

interaction) that holds A and B together. If absorption of a photon by A~B leads to an excited state (and perhaps, ultimately, to charge separation) that is mainly localized on either of the subunits, then the chemical species is supramolecular in nature. If the excited state is mainly delocalized over the whole system, then the species must be regarded simply as a large molecule. Similar arguments can be made if the complex species is oxidized or reduced. If the electron or hole is localized on either A or B, the species is supramolecular. If the electron or hole is substantially delocalized over the entire complex chemical system, then the species is best described as a large molecule.⁴

Supramolecular chemistry spans many traditional subfields of chemistry. Some areas of study include host–guest chemistry, self-assembly and self-organization, molecular sensing and recognition, transport phenomena, anion coordination, materials science, catalysis, molecular devices, photochemistry, and energy storage.

Supramolecular Photochemical Devices

In one sense, a device may be defined as a piece of equipment or a machine designed to serve a particular purpose or function. A machine usually comprises interacting components that collectively perform beneficial tasks. Both macroscopic and molecular devices, or machines, are useful for what they *do*, rather than for what they *are*. Light induced processes have been among the most widely studied phenomena in the area supramolecular device chemistry. Energy migration, induced charge separation, perturbation of polarizabilities, modification of redox potentials, and regulation of binding properties are some effects that could potentially be used to *do* something beneficial in devices that comprise photosensitive components.⁵

An increasingly important research goal is the conversion of light to chemical energy. An enormous number of photochemical molecular devices (PMDs) have been shown to collect and store light energy.⁶ Early on, most of these devices were capable of storing and delivering only a single photo-excited electron. One of the ultimate goals in this field of study is to design catalytic systems capable of delivering multiple electrons to a reactive site, as many of the uphill chemical processes are multielectron processes.⁵ Figure 2⁷ is a stylized representation of a PMD capable of delivering multiple electrons to a substrate in the presence of sacrificial electron donors.

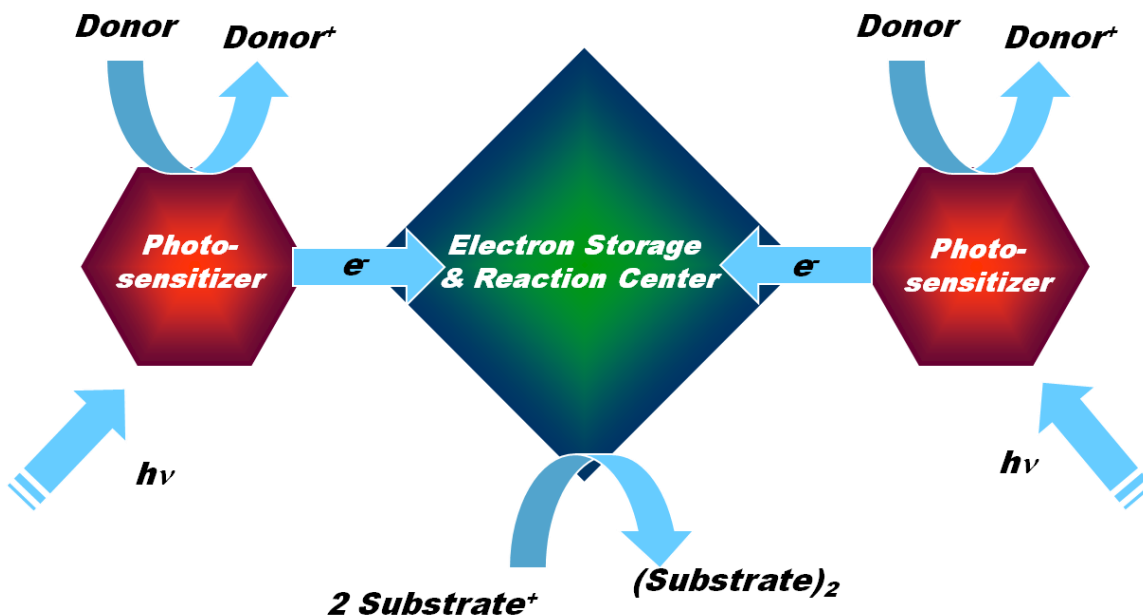


Figure 2. Schematic of PMD for Photoinduced Electron Collection and Multielectron Catalysis. Adapted from Steed and Atwood.⁷

Brewer and co-workers were the first to report a supramolecular device having the ability to perform this kind of catalysis.⁸ The Ru-Ir-Ru triad shown in Figure 3 could

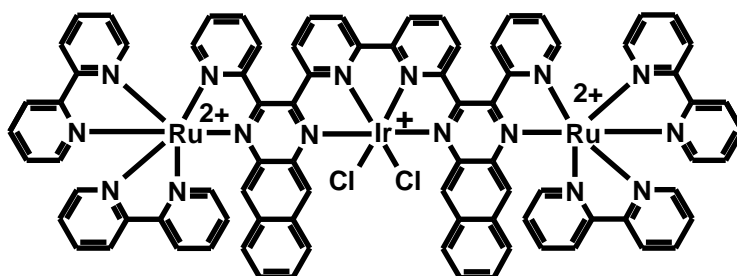


Figure 3. First Reported Supramolecular Triad Capable of Storing Multiple Photoexcited Electrons.

store two photoexcited electrons in the presence of sacrificial amine donors.

Photoexcitation of the Ru(II) units followed by double electron transfer to the Ir(III) core reduces it to Ir(I). The Ir(I), then, was capable of reducing CO₂ to formic acid in presence

of H^+ . Recently, other systems have been designed that have been able to store multiple photo-excited electrons.⁹

Robson-Type Complexes

Many syntheses of homo- and heterobimetallic complexes based on Robson-type¹⁰ tetraaminodiphenolate macrocyclic compartmental ligands (Figure 4) have been

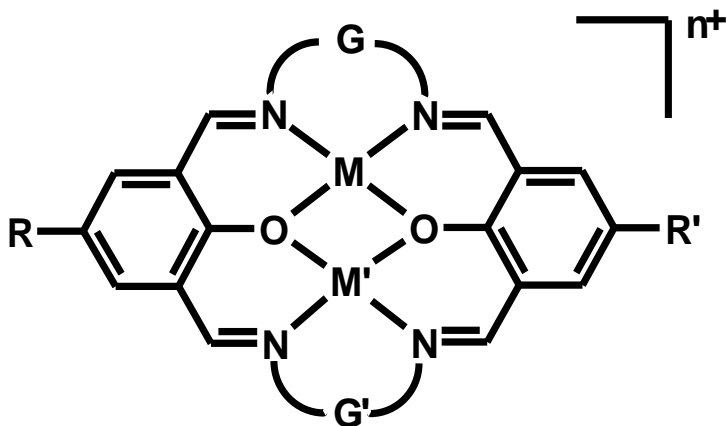


Figure 4. Generalized Representation of Cation of Binuclear Metal Complex with Robson-Type Compartmental Ligand. G and G' are generic diradicals, *i.e.*, the residues of the primary α,ω -diamines. R and R' are the 4-substituents of the phenol residues. Charge, n, is the charge on M plus the charge on M' less 2.

recently reported.¹¹ The dinuclear cores of these complexes are thermodynamically stabilized by the macrocyclic effect.¹² Although there are reported syntheses of the metal-free macrocyclic ligands¹³, the complexes are usually formed by the divalent metal-templated condensation of an appropriate primary diamine with a 4-substituted-2,6-diformylphenol. It is common that diamine residues bear additional donor groups, such as carboxylate, amino, pyridyl, or alcohol. The 4-substituents of the phenolic residues are often alkyl, usually methyl or *tert*-butyl, although other groups in this

position are known. The development of these and related types of compartmental macrocyclic ligands and their complexes has been the subject of a recent review.¹⁴ In addition to extensive physiochemical characterization, these types of complexes, along with their amino, thiophenolate, or mixed derivatives, have been used to activate small molecule substrates towards various transformations¹⁵ and have served as models of active sites of certain metalloenzymes or metalloproteins, showing activity in some biologically important reactions, simulating, for example, catalase, catecholase, and oxygenase.¹⁶ Additionally, the complexes have been used in the field of supramolecular chemistry, forming ladders, chains, or other polymetallic assemblies,¹⁷ often by bridging the bimetallic centers with neutral or charged donor species, such as bisnitrogen heterocycles, carboxylates,¹⁸ or complex anions.¹⁹

Dicopper complexes are among the most widely studied of the compounds of this general architectural form. In fact, the first reported substance¹⁰ of this description was the dicopper(II) complex where G and G' were $-(CH_2)_3-$ and R and R' were methyl. Over 130 complexes of this sort, where M and M' are copper, have been assigned a Gmelin registry number.²⁰ Many structural variations are possible and many structure–property relationships have been investigated. Magneto–structural correlations have been evaluated for several di- μ -oxo copper complexes²¹ and their isotropic exchange-coupling constants were predicted. The influence of electron-withdrawing substituents,²² attached at the 4-position of the phenol residue or attached through the diamine residue or through both residues, on exchange coupling has likewise been assessed by study of the magnetic and structural properties for several complexes. Chiral versions of these Robson-type dicopper complexes have also been synthesized and have shown utility in enantioselective

oxidative coupling reactions²³ and other asymmetric catalytic processes.^{11z} Several mixed-valence copper(II)–copper(I) species were prepared by either chemical²⁴ (sodium dithionite) or electrochemical reduction of corresponding dicopper(II) complexes. Some dicopper(I) complexes have also been prepared electrochemically.²⁵ In this study, the $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ species was reduced to the $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ species in separate one-electron processes. The intramolecular electron transfer rate of the mixed-valence species was estimated from electron paramagnetic resonance analysis.²⁵ These complexes were also studied by X-ray photoelectron spectroscopy.²⁶ Fully π -conjugated systems, derived from rigid aromatic diamines, have also been synthesized.²⁷

In one interesting synthetic variation, a tetranuclear copper complex was formed by fusing two dinuclear macrocyclic cores *via* a 1,2,4,5-tetraaminobenzene bridging group. In another modification, a tetracopper(II) complex was synthesized that comprised a Robson-type core bearing two mononuclear copper units that were covalently tethered through the diamine residues.²⁸ This complex was prepared in order to study intramolecular electron transfer as relevant to multicopper oxidase.^{11o} These are the only two reported syntheses of dinuclear copper complexes of tetraaminodiphenolate macrocyclic compartmental ligands to which other metal complexes are covalently linked.

Polypyridyl Ruthenium(II) Complexes

Polypyridyl ruthenium(II) complexes have also been extensively investigated. As early as the 1960s, the special properties of Ru(II)-polypyridine complexes began to demand attention from the photochemical community.²⁹ In contrast to the dinuclear

copper complexes, there are a great many reported substances where polypyridyl ruthenium complexes are covalently linked to other metal complexes. The complexes have been linked to additional ruthenium complexes or to complexes of other metals. These complexes have been widely used in the area of supramolecular chemistry, especially supramolecular photochemistry. Metallosupramolecular polymers, dendrimers, and self-assembled macrocycles comprising polypyridine complexes of ruthenium have all been reported.³⁰ Interest in light-harvesting species, optoelectronics, photocatalysis, and charge-separation devices has fueled much of the research in this field.³¹ An especially important use of these types of complexes is in the construction of supramolecular photo- and electrochemical devices.⁵ Many studies of electron- or energy transfer in supramolecular species have been conducted over the last 2 decades and have been well-reviewed.³² Many of the systems studied comprise polypyridyl metal complexes as both the donor and acceptor units such as the dyad shown in Figure 5.³³

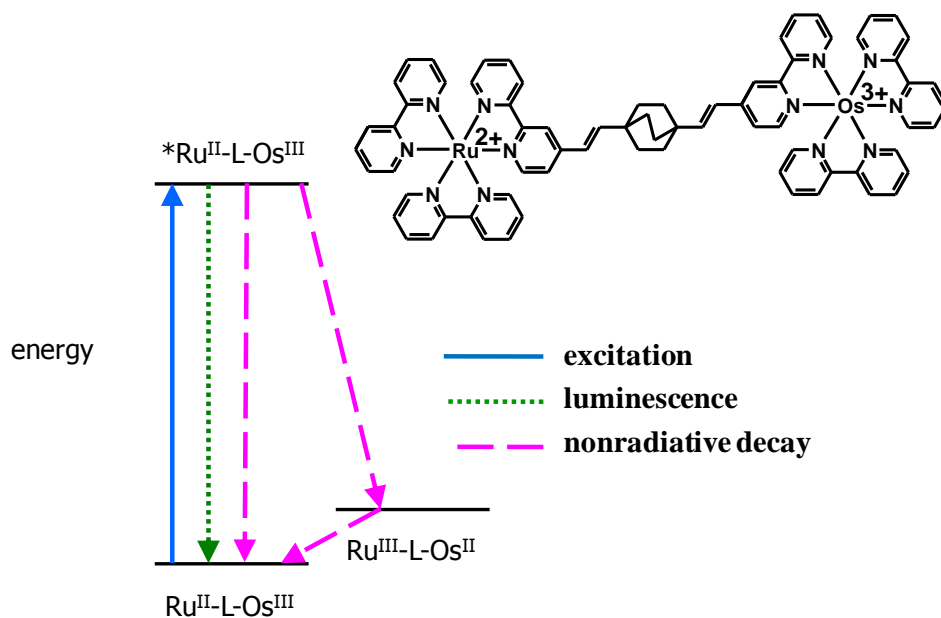


Figure 5. Energy Level Diagram for Photoinduced Energy and Electron-Transfer Processes in a Supramolecular Ru(II)/Os(III) Dyad.

In these types of systems, and as illustrated by the specific example in Figure 5, the species that undergoes photo-excitation is often a $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) moiety and the energy acceptor is often an $[\text{Os}(\text{bpy})_3]^{2+}$ unit.⁴ The related 1,10-phenanthroline (phen) complexes are also similarly used. The use of $[\text{Ru}(\text{tpy})_3]^{2+}$ and $[\text{Os}(\text{tpy})_3]^{2+}$ units (tpy = 2,2':6',2''-terpyridine) as donors and acceptors, respectively, is also well-known. The terpyridine moieties are frequently further substituted at the 4'-position. Additionally, it is quite common to connect either $[\text{Ru}(\text{bpy})_3]^{2+}$ -type (*tris*(bpy)) or $[\text{Ru}(\text{tpy})_2]^{2+}$ -type (*bis*(tpy)) ruthenium(II) photosensitizing units to phthalocyanines or metallated or non-metallated porphyrins.³⁴ Much of the research in this area was rooted in gaining a better understanding of natural photosynthetic processes. The *tris*(bpy) and *bis*(tpy) ruthenium(II) systems each possess advantages and disadvantages relative to each other. The bipyridine systems have a *much* longer lived excited state, thus enabling the study of energy transfer over long distances. The terpyridine systems are usually considered more desirable from a structural point of view.^{5,35}

Known Ruthenium/Copper Species

Several substances have been reported where polypyridyl ruthenium(II) complexes are covalently linked to a copper complex.³⁶ Particularly interesting were systems where 4,5-diamino-1,10-phenanthroline (as the free amine or complexed to $\text{Ru}(\text{bpy})_2$ or $\text{Ru}(\text{phen})_2$) was condensed with 2 equivalents of a salicylaldehyde or a picolinate derivative.³⁷ In some of these systems, photochemical studies suggested that the polypyridyl ruthenium(II) excited state was effectively quenched by intramolecular electron- or energy transfer to the copper unit. Recently, a novel donor–acceptor system

was synthesized that comprised a *tris*(bpy)-type ruthenium(II) complex covalently linked to the secondary face of a β -cyclodextrin that had its primary face capped with a hydroxo bridged dinuclear copper(II) moiety.³⁸ The rate of the intramolecular photoinduced electron transfer from the excited ruthenium to the copper center was estimated from luminescence lifetime studies. To date, however, there has been no reported synthesis of any polypyridyl ruthenium(II) complex being covalently linked to a Robson-type dinuclear copper(II) complex.

Project Goal

In light of the extremely rich photophysical and redox properties of polypyridyl ruthenium(II) complexes, especially in regards to electron- or energy transfer; and in light of the unique electronic and catalytic behavior of Robson-type dinuclear copper(II) complexes, the construction of a polynuclear array that comprises both these moieties is a worthwhile synthetic goal. This work reports on the design and syntheses of these new hybrids. It is expected that combinations of the two types of complexes will exhibit interesting photo- and electrochemical properties, possibly allowing the observation of a 2-electron transfer from ruthenium to copper.

CHAPTER 2

RESULTS AND DISCUSSION

Design Rationale

Early on, it was decided that, at least initially, a symmetrical supermolecule would be preferred from the standpoint of synthetic simplicity. With that in mind, two basic polynuclear complex architectures were conceptualized, in both of which the dicopper macrocycle was the central feature of the array. The first concept, **I**, illustrated graphically in Figure 6, involves attachment of the polypyridyl ruthenium(II) units at the

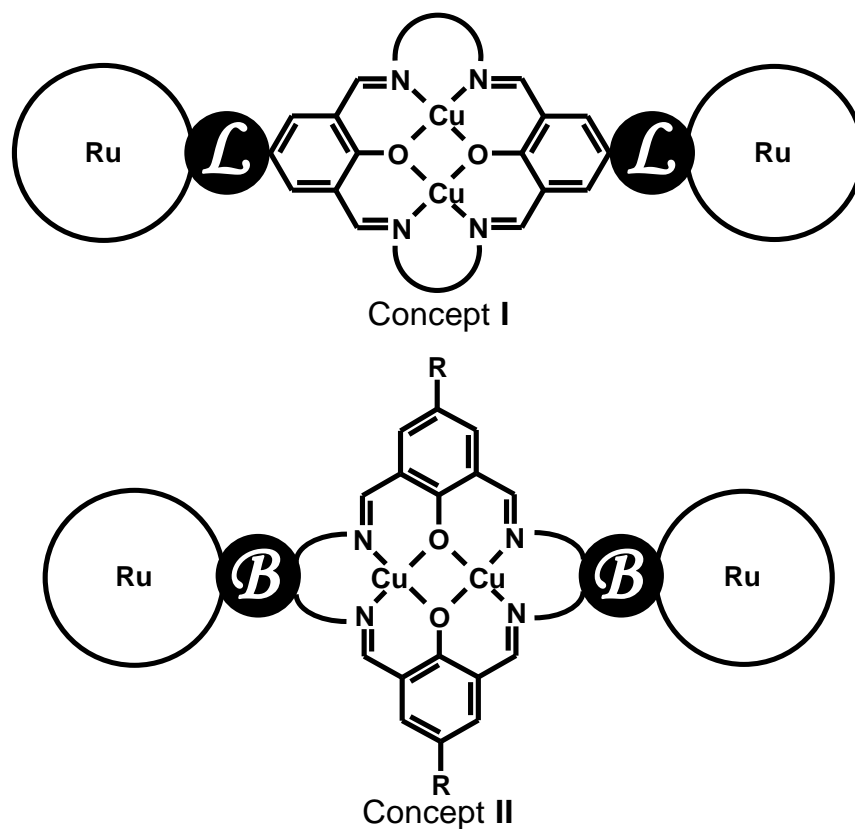


Figure 6. Stylized Representation Illustrating Different Modes of Attachment of Ruthenium(II) Units to Dicopper(II) Complex. (Ru) 's are either $[Ru(tpy)_2]^{2+}$ -type or $[Ru(bpy)_3]^{2+}$ -type complexes. **L** and **B** are generic linking groups.

4-position of the phenolic residue of the dicopper(II) macrocycle through some generic linking group, \mathcal{L} . It was envisaged that \mathcal{L} , at least in the first iterations, should possess a π -system in conjugation with the macrocycle and the polypyridine ligands. Some obvious choices for \mathcal{L} would include catenated phenylene or catenated acetylene units. \mathcal{L} could also comprise conjugated olefin units, certain amide or imide moieties, or \mathcal{L} could simply be a single covalent bond.

A second general concept, **II**, that would meet these specific synthetic goals is also shown in Figure 6. Here, the ruthenium(II) units are linked to the copper complex through the diamine residue *via* a generic bridging ligand, \mathcal{B} . Again, it was expected that \mathcal{B} should provide a continuous π -system that would bridge the copper and ruthenium complexes. An aromatic diamine comprising or conjugated to a polypyridine would be suitable. The ruthenium units in **I** or **II** could be based on either substituted *bis*(tpy) or *tris*(bpy) complexes.

Of the two basic proposed architectures discussed, most of the initial synthetic activity herein reported was directed towards triads of type **I** where the ruthenium units were *bis* terpyridine complexes.

Plausible Chemistry to Desired Triads

Known Routes to 4'-Substituted-2,2':6',2''-Terpyridines

4'-Substituted-2,2':6',2''-terpyridines (or further substituted terpyridines) have been accessed by classical methods and by Pd(0) catalyzed cross-coupling reactions, *e.g.*, Suzuki-Miyaura, Stille, and Negishi arylations or hetarylations.³⁹ Additionally, cross-

coupling reactions of halogenated or borylated terpyridines to obtain further substitution of the terpyridine moiety are also known.⁴⁰

Known Routes to 4-Substituted-2,6-Diformylphenols

Syntheses of 4-substituted-2,6-diformylphenols have been realized, among other methods, by direct diformylation of the 4-substitutedphenol by the Duff reaction.⁴¹ These compounds have also been synthesized by *via* di-hydroformylation of the phenolate with formaldehyde to the 2,6-dimethanol⁴² followed by oxidation to the dialdehyde.⁴³

Known Suzuki Chemistry to Couple Phenols and Formylphenols

Although Suzuki couplings of 2,6-diformylphenols are not known, there are reports of coupling free and protected phenols. The phenol or protected phenol can be either the halogenated⁴⁴ or the borylated⁴⁵ (both boronic acids and boronic esters are known) partner. More closely related to the present study, successful Suzuki couplings of both halogen- and boron-substituted salicaldehydes have been reported, as well as Miyaura borylations of halogenated salicaldehyde derivatives.⁴⁶ In some cases the phenol of the salicaldehyde had been protected.

Possible Routes to the Desired Tetranuclear Bimetallic Complexes

It was expected that a terpyridine-functionalized diformylphenol should be accessible by one of the routes described above. This terpyridine-functionalized dialdehyde could then be treated with (tpy)RuCl₃ or with (X-tpy)RuCl₃ (X-tpy = a 4'-substituted-2,2':6',2''-terpyridine) to give a ruthenium(II) complex-functionalized

dialdehyde. Further reaction with an appropriate diamine in the presence of a cupric salt should give the desired type **I** tetranuclear triad.

Cross-coupling of bromo-substituted or borylated polypyridine ruthenium(II) complexes is well-known.⁴⁷ Cross-coupling a halo- or boron-functionalized $[\text{Ru}(\text{tpy})_2]^{2+}$ -type complex with an appropriately substituted diformylphenol would be another feasible synthetic pathway to the ruthenium(II) complex-functionalized dialdehyde.

Additionally, in theory at least, cross-coupling of a preformed dibrominated (or diborylated) copper(II) macrocycle with 2 equivalents of a monoborylated (or monobrominated) ruthenium(II) complex might be another possible route to the desired tetranuclear bimetallic triads. The Suzuki coupling, however, of copper(II) complexes has not been reported.

Specific Synthetic Targets

The bulk of the synthetic activity presented here was aimed toward type **I** triads where the ruthenium units were $[\text{Ru}(\text{tpy})_2]^{2+}$ -type complexes. Some progress toward the synthesis of type **I** triads where the ruthenium units were $[\text{Ru}(\text{bpy})_3]^{2+}$ -type complexes was also realized. Additionally, some work was directed toward type **II** triads.

All the targeted triads that were pursued in this work are shown in Figure 7. In compounds **1a** and **1b**, the terminal ligand of both the ruthenium(II) complexes is 4'-(4-methylphenyl)-2,2':6,2''-terpyridine ($\text{CH}_3\text{-}\phi\text{-tpy}$, where $\phi = 1,4\text{-phenylene}$). In compound **2**, each terminal *tris*(bpy)-type ruthenium(II) unit is attached to the dicopper(II) core through the 5-position of a bipyridine ligand. Compounds **3** use 4,5-diamino-1,10-phenanthroline as the diamine from which the macrocycle is formed and its diimine

residues are the bridging ligands that link the dicopper(II) center with the two ruthenium(II) centers.

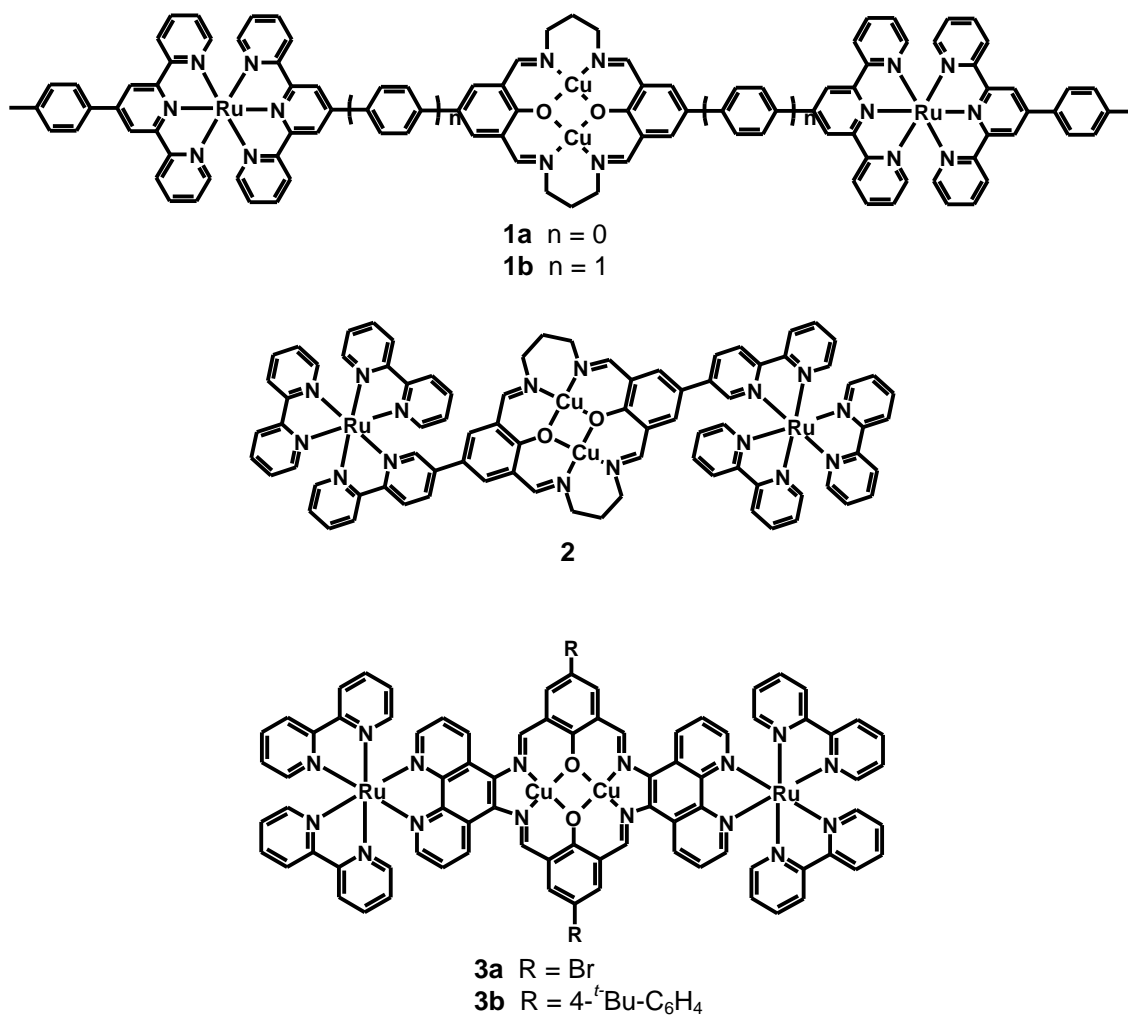


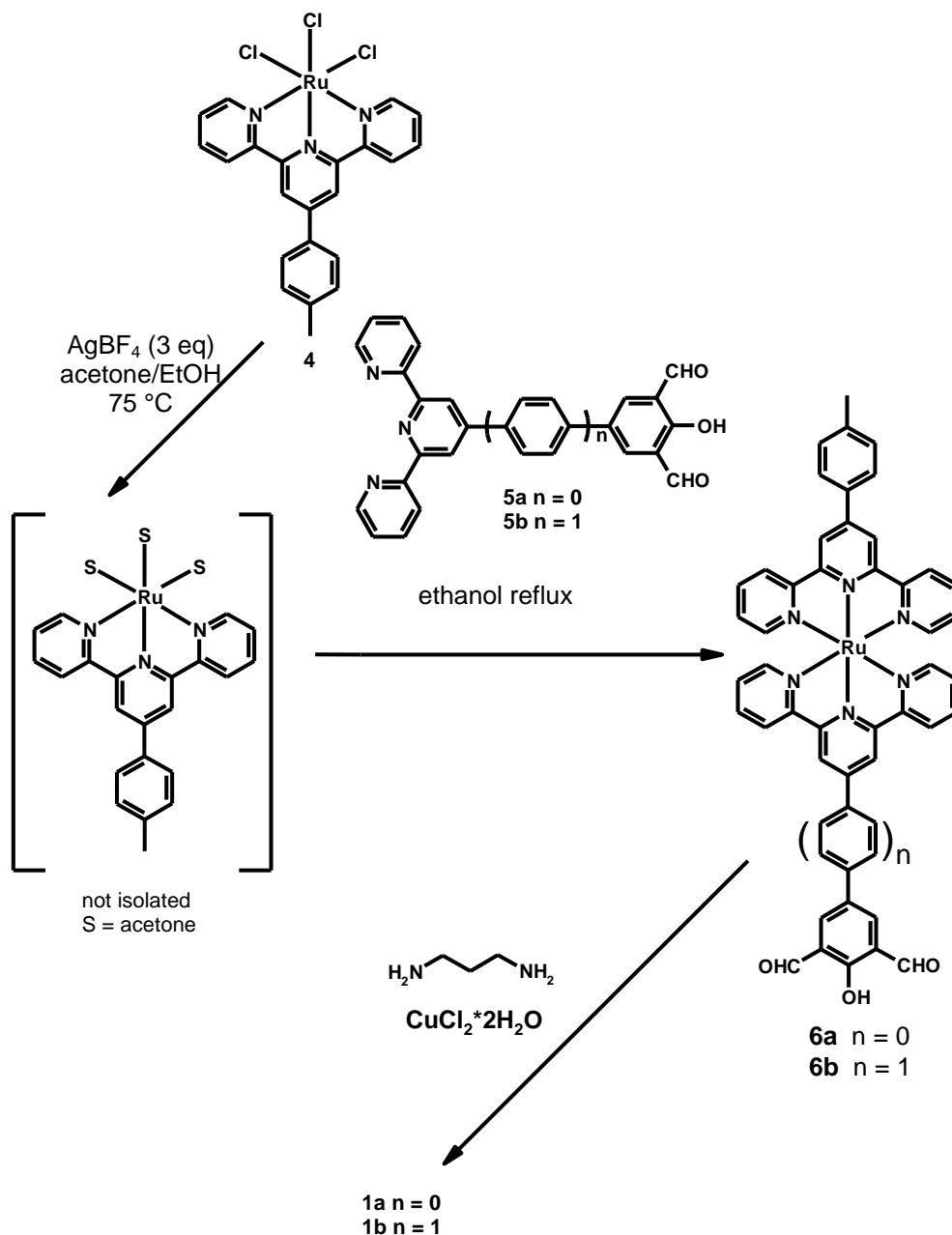
Figure 7. Targeted Supramolecular Triads Pursued in the Course of this Work. Counteranions and charges on the complexes are omitted to simplify the graphic.

Synthetic Strategies Toward Preparation of Triads **1**

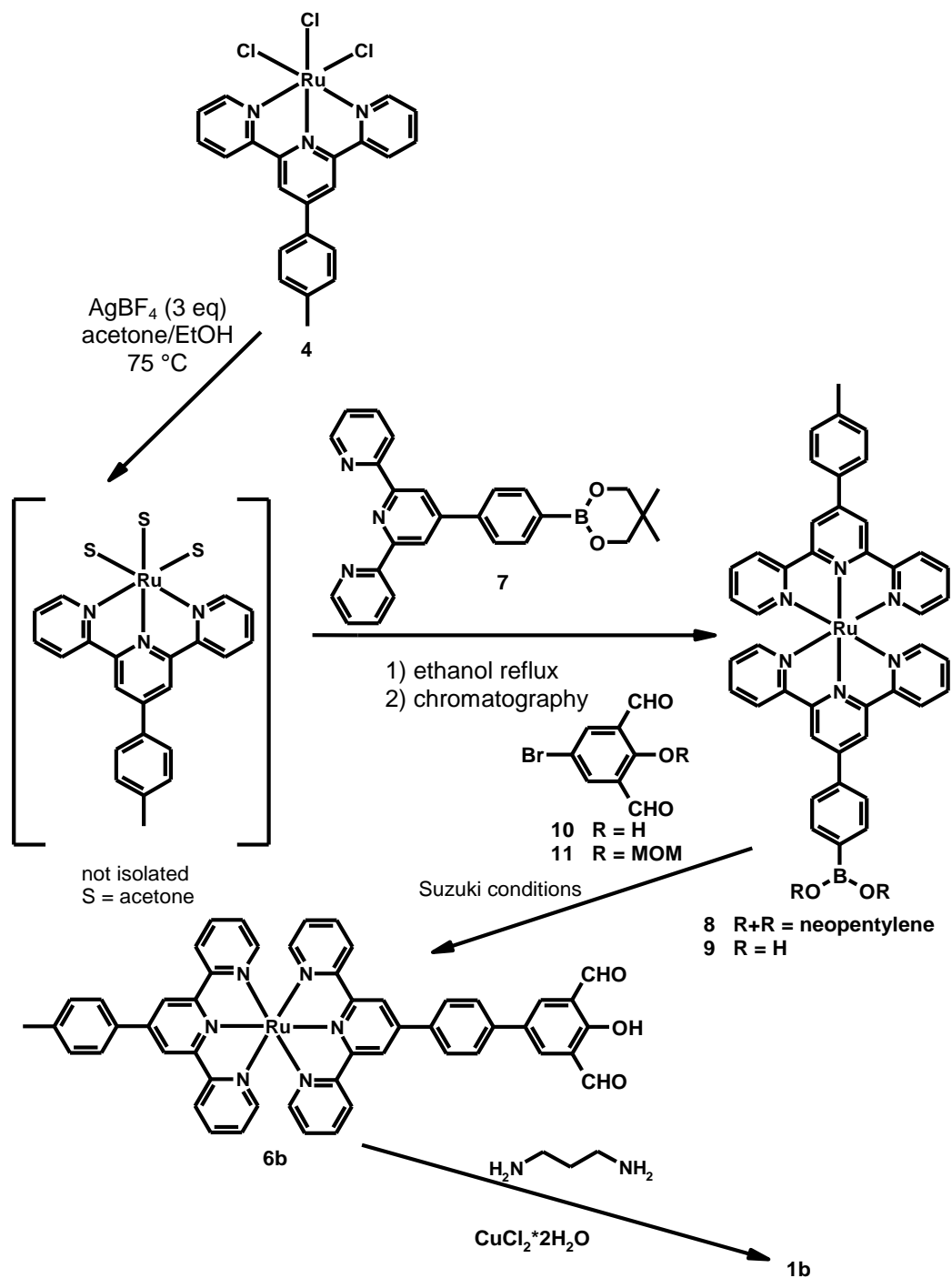
Three related approaches to the syntheses of triads [**1**]⁶⁺ are outlined in Schemes

1-3. The proposed route shown in Scheme 1 (Method A) involved complexation of

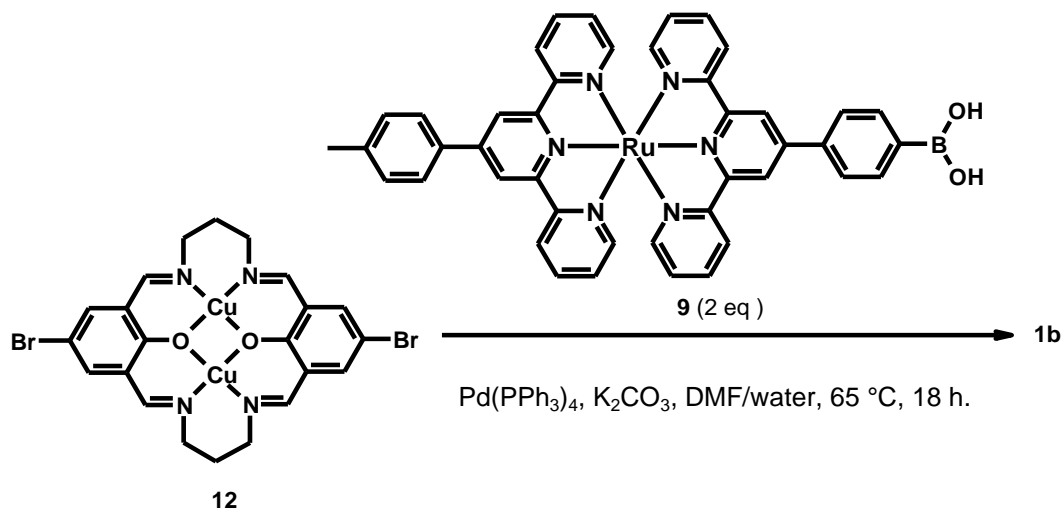
Scheme 1. Proposed synthetic route (Method A) to targeted supramolecular triads [**1**]⁶⁺. Counteranions and charges on the complexes are omitted to simplify the graphic.



Scheme 2. Proposed synthetic route (Method B) to targeted supramolecular triad **[1b]**⁶⁺. Counteranions and charges on the complexes are omitted to simplify the graphic.



Scheme 3. Proposed synthetic route (Method C) to targeted supramolecular triad $[\mathbf{1b}]^{6+}$. Counteranions and charges on the complexes are omitted to simplify the graphic.



$(\text{CH}_3\text{-}\phi\text{-tpy})\text{RuCl}_3$ **4** to preformed terpyridine-functionalized diformylphenols **5** to give the ruthenium complex-functionalized diformylphenols **6**. The required dialdehydes **5** could be formed by Pd(0) catalyzed cross-coupling or other reactions.

The proposed route to $[\mathbf{1b}]^{6+}$ outlined in Scheme 2 (Method B) differs from Method A in that **4** is first complexed with borylated terpyridine **7** to give borylated ruthenium complex **8** (or **9**). Complex **8** (or **9**) could then be heterocoupled under Suzuki conditions with brominated diformylphenol **10** (or a protected version of **10**) to give **6b**.

Another approach to triad $[\mathbf{1b}]^{6+}$ is shown in Scheme 3 (Method C). In this proposed pathway, synthesis of $[\mathbf{1b}]^{6+}$ depended on successful heterocoupling of dibrominated dicopper(II) complex **12** with 2 equiv of borylated ruthenium complex **9**.

Towards Preparation of [**1b**]⁶⁺ by Coupling Preformed Ruthenium and Copper
Complexes (Method C)

Synthesis of Diformylphenol **10**

Compound **10** was synthesized by a modified Duff reaction closely following Lindoy's reported procedure⁴¹. In this modification, the normally-used glacial acetic acid is replaced with anhydrous trifluoroacetic acid as solvent and proton source. The synthesis of this compound proceeded smoothly in most preparations, although the reaction time was increased over that reported in the literature to ensure that all of the monoformylated intermediate product was cleanly converted to the desired dialdehyde.

Synthesis and Characterization of Copper Complex **12**

The dibromo-fuctionalized copper complex **12** was obtained as a green powder as its dichloride by reaction of **10** with cupric chloride dihydrate and 1,3-diaminopropane in methanol. Being paramagnetic, the complex could not be well characterized by NMR, however elemental analysis (% CHN, calculated: C, 34.48; H, 3.16; N, 7.31; found: C, 34.52; H, 2.83; N, 7.10) was in reasonable agreement with the theoretical expectation.

The complex was further characterized by mass spectral analysis. The full scale electrospray ionization mass spectrum (ESIMS) of the isolated complex is shown in Figure 8. The expanded region shown in Figure 9 clearly indicates a doubly charged species because the C-13 isotope peak appears at m/z 328.4, 0.5 m/z units higher than the molecular ion at m/z 327.9. All singly charged species containing carbon have their C-13 isotope peak appear 1 m/z unit higher than their molecular ion. Figure 9 also shows the

computer generated theoretical isotope pattern which is essentially identical to that of the desired molecular formula. This is a very definitive isotopic cluster that supports the

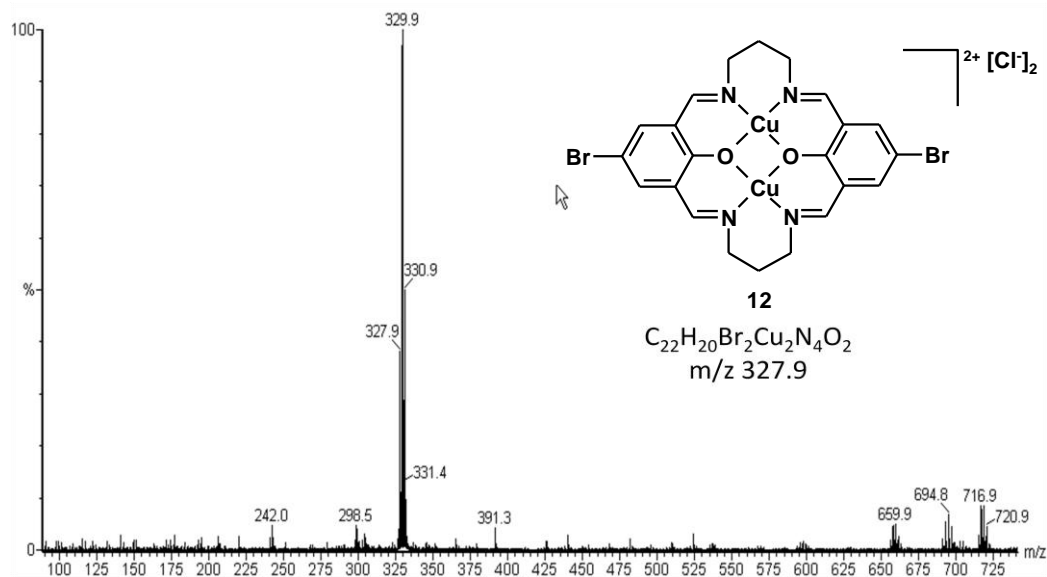


Figure 8. Full Scale Positive Ion Electrospray Mass Spectrum of Copper Complex **12**. Base peak is for doubly charged ion, M^{+2} .

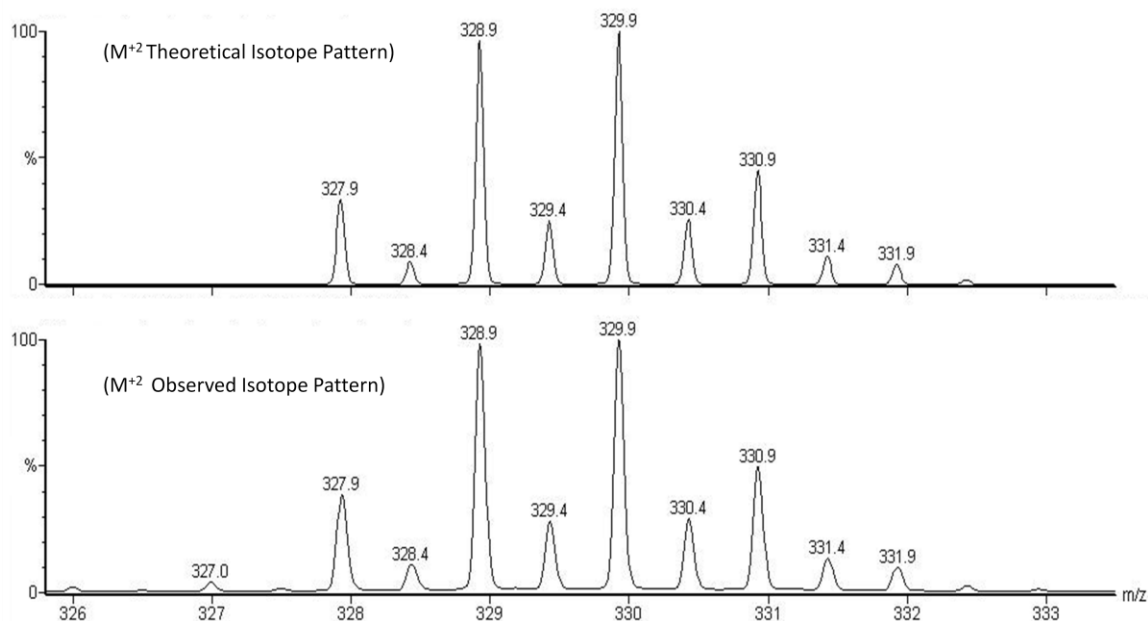


Figure 9. Expanded Positive ion Electrospray Mass Spectrum for Doubly Charged Molecular Ion, M^{+2} , of Copper Complex **12**. Top trace, theoretical isotope pattern; bottom trace, observed isotope pattern.

presence of two bromines and two copper atoms in the molecular structure. Both bromine (^{79}Br 50.4%, ^{81}Br 49.5%) and copper (^{63}Cu 69.1%, ^{65}Cu 30.9%) have significant concentrations of stable isotopes.

Figure 10 shows an expanded scale mass spectrum for the higher m/z region of the spectrum that also supports the proposed structure. The $(\text{M}+\text{Cl})^+$ isotope cluster is a singly charged ion in which the doubly charged cation is counterbalanced by the

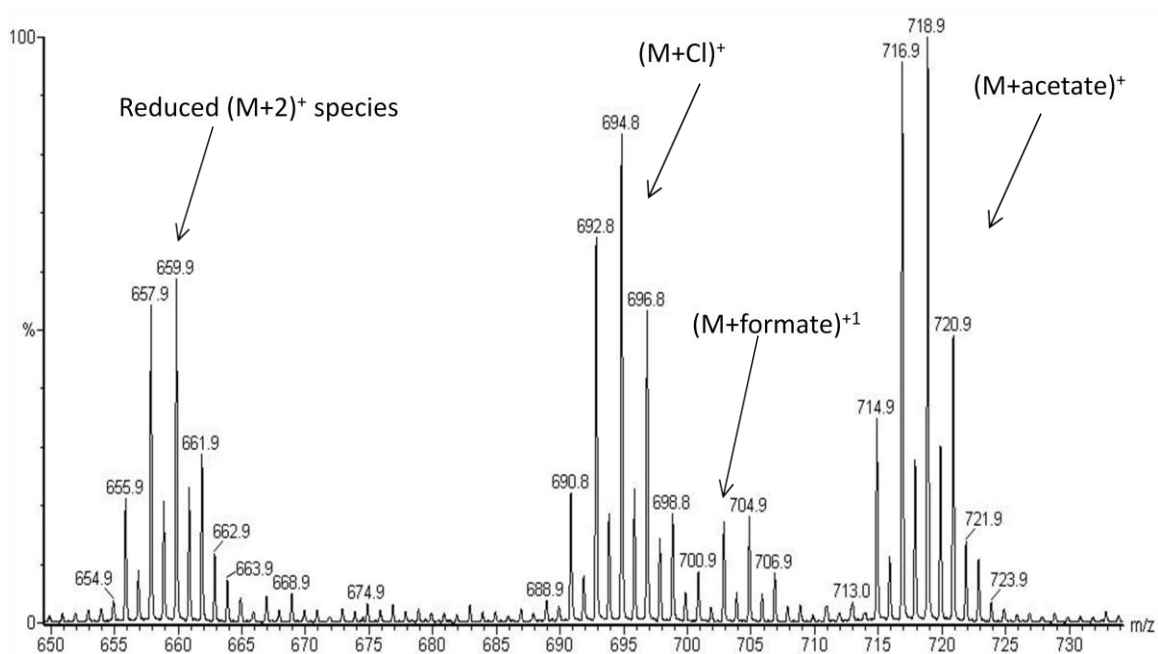


Figure 10. Expanded Positive Ion Electrospray Mass Spectrum of Copper Complex **12** Showing Singly Charged Region of Spectrum.

chloride anion. The formate and acetate adducts are due to anion contamination of the mass spectrometer source by high levels of buffer routinely used in liquid chromatography-mass spectrometry analyses. The isotopic cluster at m/z 655.9 is an artifact of the positive ion electrospray analyses. Apparently one of the $\text{Cu}(\text{II})$ ions in the species is being reduced. This ion disappears when the electrospray needle potential was

reduced from 3500 to 2000 V. Frequently organometallic species can undergo electrochemical reactions during electrospray analyses as a function of needle potential.

The UV-vis spectrum (Figure 11) exhibited bands that would be expected to arise from the $d \leftrightarrow d$ transitions. The positions of these bands were similar to those reported for the original 4,4'-dimethyl substituted complex; additionally the molar absorptivity (ϵ) at the $d \leftrightarrow d$ band maximum was on the same order, *i.e.*, about 90 at 606 nm for the dibromo- compared to 80 at 606 nm for the original dimethyl-functionalized complex.¹⁰

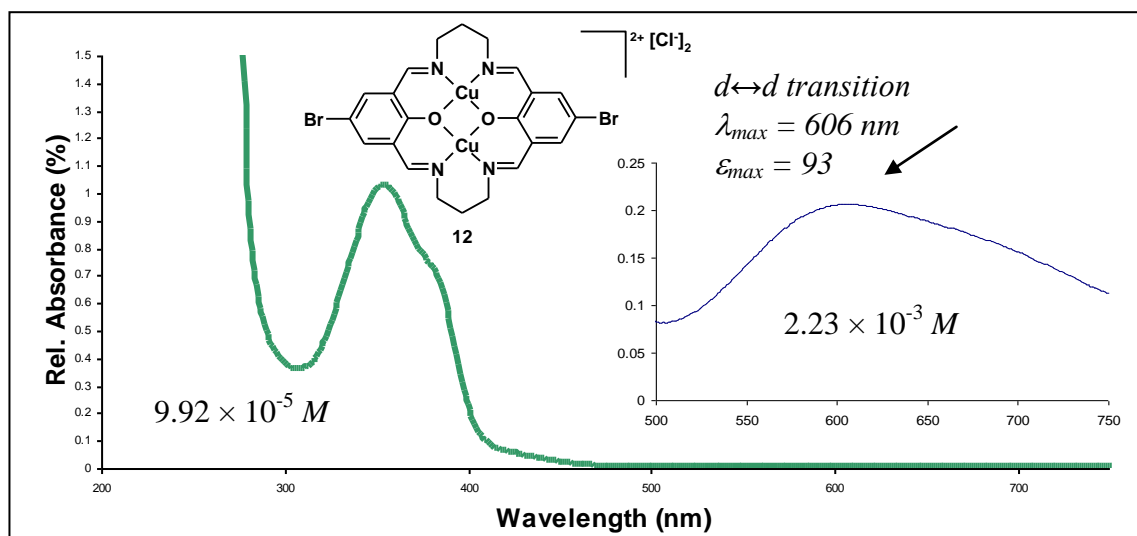


Figure 11. UV-Vis Spectrum of Copper Complex 12. The solvent was water.

Synthesis of Zinc Complex 13

As a further test of the complexation procedure, the binuclear zinc complex 13 was similarly formed by reaction of 10 with zinc tetrafluoroborate hydrate and 1,3-diaminopropane in refluxing methanol. The diamagnetic complex was obtained as a yellow crystalline solid and its 1H NMR spectrum (Figure 12) supported the proposed macrocyclic structure.

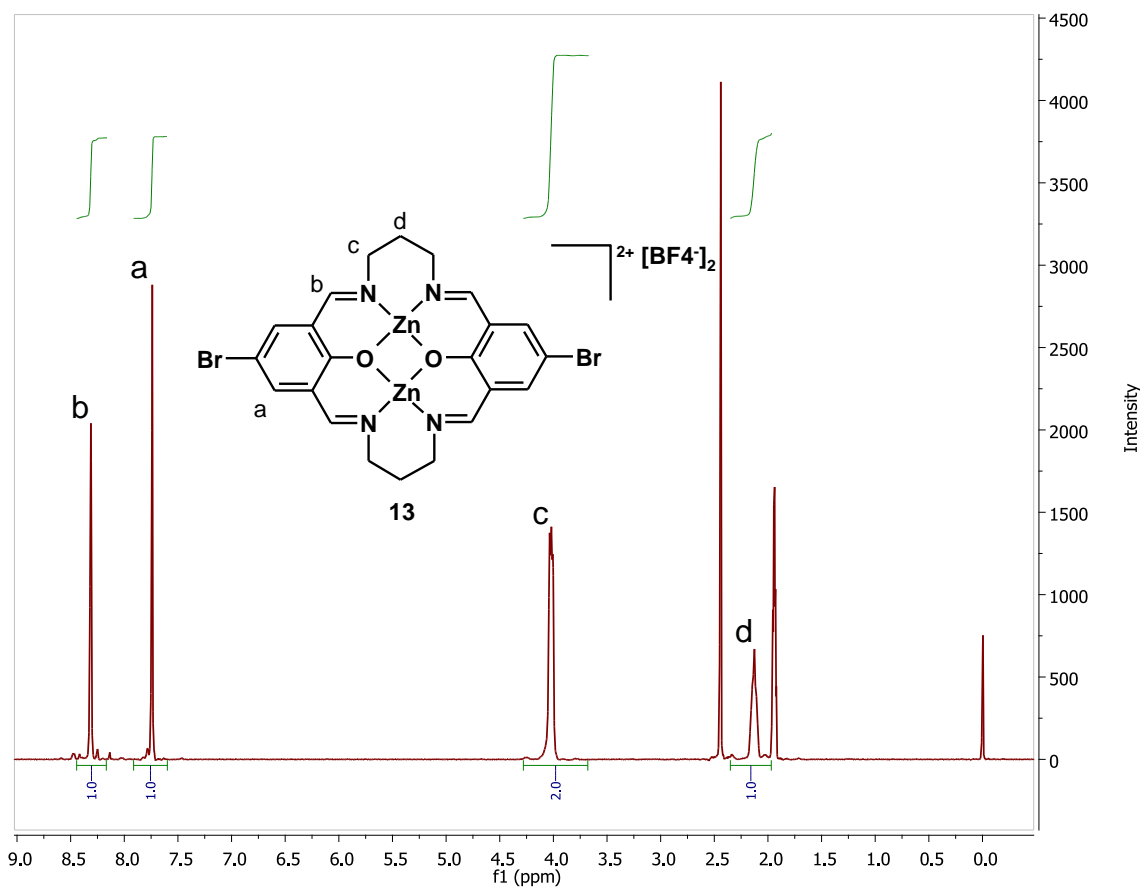


Figure 12. 300 MHz ¹H NMR Spectrum of Zinc Complex **13**. The solvent was deuterated acetonitrile.

Attempted Suzuki Coupling of Copper Complex **12**

Before endeavoring to couple copper complex **12** with ruthenium complex **9** (as in Scheme 2), Suzuki coupling of **12** with the commercially available 4-*tert*-butylphenylboronic acid was attempted under various reaction conditions. In all these cases water was used as the solvent, with or without addition of a cosolvent (acetone or DMF). The reaction temperature ranged from ambient to 65 °C. No desired heterocoupled product was observed by mass spectrometry in any case. In some of the higher temperature cases, the mass spectral analyses suggested that palladium may have

been incorporated into the macrocycle. In light of these results, no experiments were conducted to attempt the cross-coupling of the dicopper(II) complex **12** with ruthenium(II) complex **9**.

Towards Preparation of $[1b]^{6+}$ by Coupling Preformed Ruthenium Complex **8** with **11**

(Method B)

Synthesis of and Attempted Suzuki Coupling of Ruthenium Complex **8**

Ruthenium complex **8** was obtained from **4** and **16** (scheme 6) according to the literature procedure^{47c} and was purified by column chromatography. Upon chromatography, the neopentyl glycol ester is cleaved and therefore the complex is isolated as the boronic acid **9**. However, on a first and single attempt, reaction of **9** (Scheme 6) with the MOM-protected 2,6-diformyl phenol **11** under Suzuki conditions did not yield the desired complex **6b**.

Towards Preparation of $[1]^{6+}$ from Preformed Terpyridine-Functionalized

Diformylphenols (Method A)

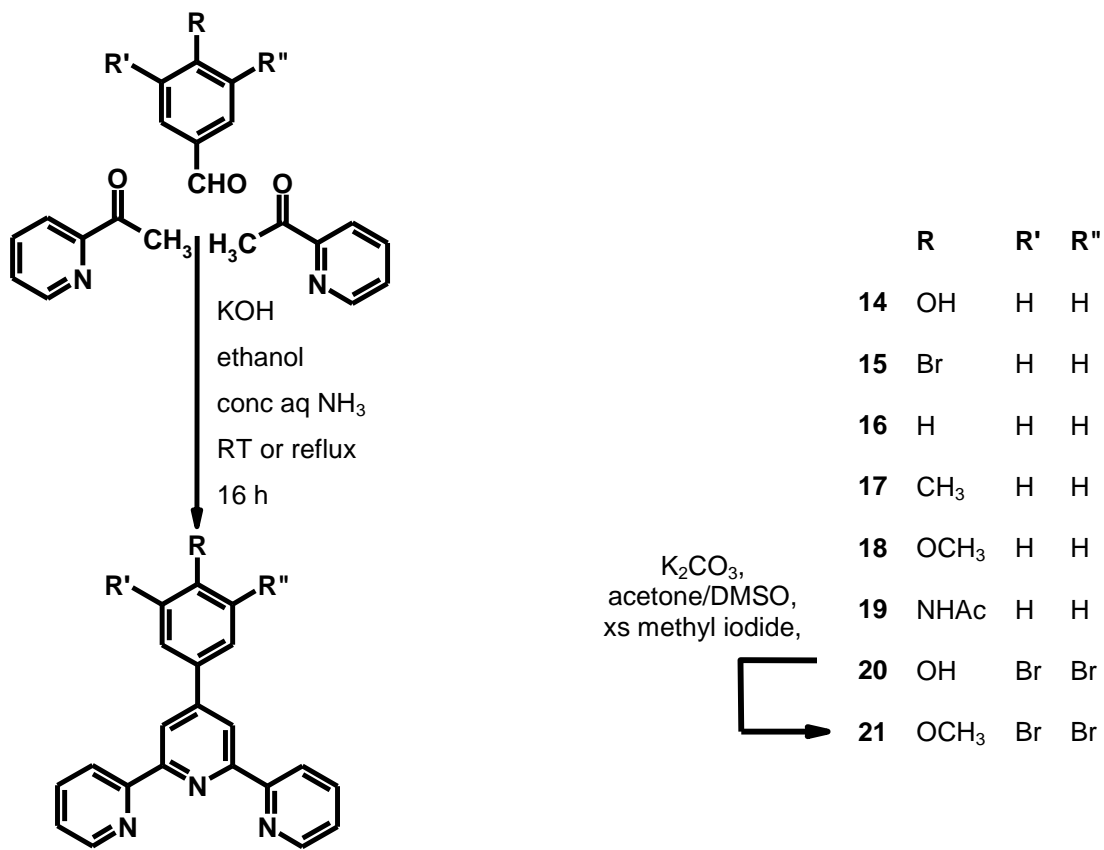
This preferred synthetic route (Scheme 1) to the desired triads **1a** and **1b** involved first synthesizing terpyridine-functionalized diformylphenols. Thus, diformylphenols **5a** and **5b** were initial synthetic targets. It was reasoned that having the preformed terpyridine-functionalized diformylphenols as available common intermediates would allow access to a number of different triads **1** by changing the terminal terpyridines or the diamines. This semicombinatorial approach would allow evaluation of structure–property relationships with relative ease. Of course, if one wished to vary the distance

between the ruthenium and copper centers, this would necessitate the synthesis of new terpyridine-functionalized diformylphenols **5** with differing numbers of interposed 1,4-phenylene units. Hence, the syntheses of dialdehydes **5** were attempted by several routes.

Preparation of Terpyridines Toward the Synthesis of Compound **5a**

The first attempt to synthesize terpyridine-functionalized diformylphenol **5a** required 4'-(4-hydroxyphenyl)-2,2':6',2''-terpyridine (OH- ϕ -tpy) **14** as starting material. Compound **14**, along with several other 4'-substituted-2,2':6',2''-terpyridines, were synthesized in modest yield using a modified Kroenkhe synthesis by a slight alteration to a reported literature procedure⁴⁸ as shown in Scheme 4. Conversion of compound **14**

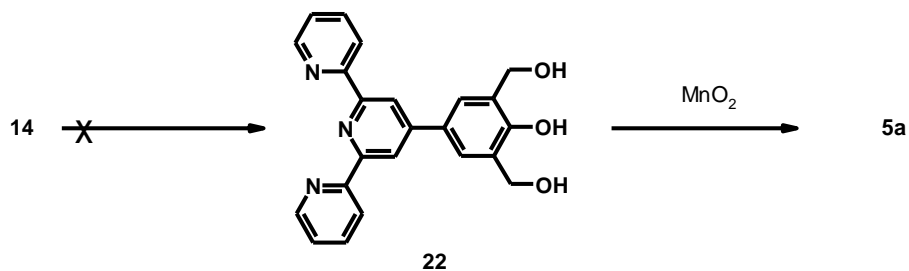
Scheme 4. Synthesis of selected terpyridines.



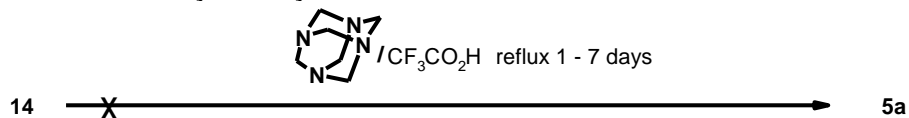
to **5a** was attempted *via* various synthetic pathways. These proposed synthetic routes are given in Scheme 5. Scheme 5 also shows other attempted routes to **5a** from terpyridines **18**, **20** and **21** and one path from 4-hydroxybenzaldehyde.

Scheme 5. Attempted routes to prepare terpyridine-functionalized dialdehyde **5a**.

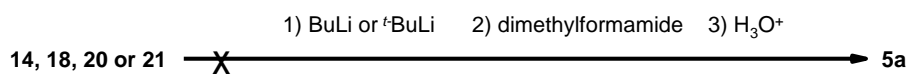
Dihydroformylation followed by oxidation to the dialdehyde:



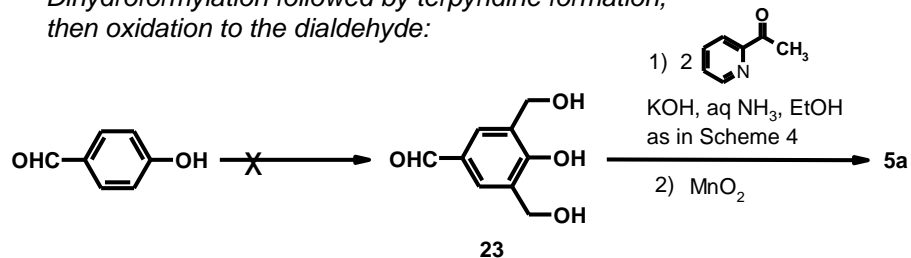
Direct diformylation by Duff reaction:



Dilithiation followed by diformylation with DMF:



Dihydroformylation followed by terpyridine formation, then oxidation to the dialdehyde:



Attempts to Form **5a** by Dihydroformylation Followed by Oxidation to the Dialdehyde

Many syntheses of 4-substituted-2,6-diformylphenols from the corresponding 4-substituted-2,6-hydroxymethylphenols are known. These dimethanols can be accessed from the 4-substituted phenols. Often the phenols are substituted at the *para* position by an alkyl group. There have been a few reports where aryl groups or electron-withdrawing groups at this position gave successful conversion to the dimethanol.⁴⁹ No desired dihydroformylated terpyridine product **22** was obtained after treatment of **14** with 37 % formaldehyde in aqueous base at 40 to 50 °C or at room temperature after extended reaction time (4-20 d). Terpyridine **14** appeared to exhibit low solubility in the reaction medium in this temperature range. The lack of reaction could also possibly be attributed to the electron-withdrawing nature of the terpyridine moiety.

Attempts to Form **5a** by Duff Reaction

Direct diformylation of **14** was attempted using Lindoy's⁴¹ modified Duff reaction in anhydrous trifluoroacetic acid. In this reaction, the phenolic substrate and hexamethylenetetramine (HMTA) are refluxed together for several hours (even up to 4 - 9 d for aryl substituted phenols⁵⁰) then the formed adduct is decomposed in aqueous acid to give the dialdehyde. Several attempts were made to effect the transformation *via* the Duff reaction, varying the time at reflux from 1 to 7 d. On every attempt, dark-colored mixtures were recovered that gave complex broadened ¹HNMR spectra. In some cases there were broad peaks in the region where aldehydic protons might be expected (see Appendix D). The inefficiency of this reaction could perhaps also be ascribed to the electron-withdrawing nature of the terpyridine, which is likely intensified in acid media.

Attempts to Form **5a** by Dilithiation Followed by Diformylation with DMF

Aryl aldehydes are often readily accessible from aryl lithiums. Synthesis of **5a** by formation of the requisite dilithiated species at low temperature, followed by reaction with dimethylformamide and acidic workup appeared to be a possible route to the desired dialdehyde. Several attempts were made to di-*ortho*-lithiate compound **14** and the methoxy protected derivative **18**. Di-*ortho*-lithiation of phenols or anisoles is not known, but because **14** was in hand and **18** was readily accessible, the experiments were deemed worthwhile even without literature precedent. However, neither **14** nor **18** gave any desired **5a** after reaction with alkylolithiums at 0 °C or -78 °C after subsequent quenching with DMF. Addition of tetramethylethylenediamine (TMEDA) did not appear to improve the fruitfulness of the reaction. Formation of the dilithio compounds was also attempted *via* lithium-halogen exchange. Synthesis of a 2-methoxy-1,3-benzenedicarbaldehyde from the corresponding 2,6-dibromoanisole is a known reaction.⁵¹ Compounds **20** and **21** were synthesized and subjected to the usual reaction conditions in attempts to form **5a**. Again, adjustment in temperature (0 °C or -78 °C), molar excesses of alkyl lithium reagent (2 to 5 eq) or use of additives (with or without TMEDA) did not appear to improve the reaction very much. In one attempted preparation, multiple peaks were noted in the ¹HNMR spectrum (see Appendix D) that might have indicated the presence of formylated species.

Attempt to Form **5a** From 4-Hydroxybenzaldehyde

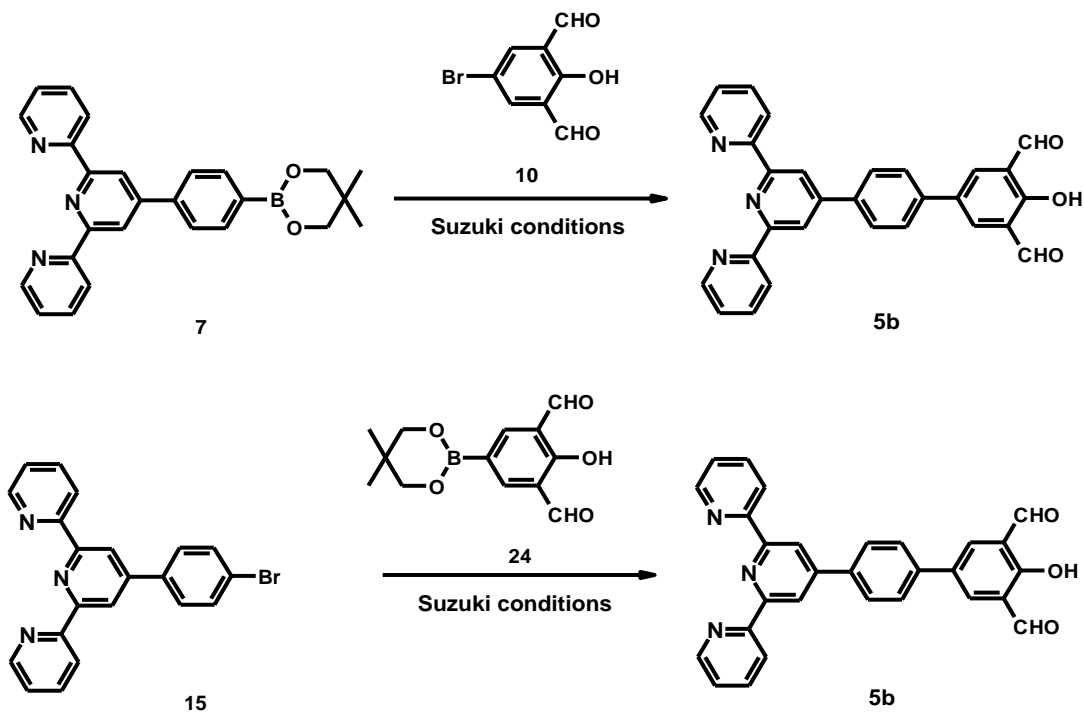
Additionally, an attempt was made to synthesize **5a** by reaction of 4-hydroxybenzaldehyde with formaldehyde in aqueous base at elevated temperature. In

this attempt, the literature conditions⁵² used for the conversion of 4-chlorophenol to the 2,6-dimethanol were adopted. It was believed if dimethanol **23** could be successfully synthesized, then the terpyridine forming reaction (shown in Scheme 4) should proceed readily to give **22**, which could in turn be oxidized to **5a**. Under those prescribed reaction conditions, however, 4-hydroxybenzaldehyde was recovered in quantity. The formyl group apparently deactivates the phenolate ring against electrophilic attack by formaldehyde.

Preparation of Compound **5b** and Related Reactions

Because attempts to synthesize **5a** were met with limited success, attention was turned to the formation of **5b**. Proposed routes to **5b**, illustrated in Scheme 6, depended

Scheme 6. Proposed routes to terpyridine-functionalized dialdehyde **5b** via Suzuki coupling.



on successful cross-coupling of borylated terpyridine **7** with **10** or cross-coupling of **15** (Br- ϕ -tpy) with **24**. It was desired that either **10** or **15** could be converted to the corresponding boron reagent by the Miyaura reaction. The strong preference was to form the boronic ester **24** (or the corresponding boronic acid) from diformylphenol **10**. This would perhaps allow coupling of either halo-substituted terpyridines or halo-substituted bipyridines with the borylated dialdehyde.

Borylation of **10** to **24** and Subsequent Attempts to Cross-Couple with **15**

Unfortunately, borylation of **10** did not occur to an appreciable extent when the diformylphenol was reacted with bis(neopentyl glycolato)diboron (B_2neo_2) under standard Miyaura conditions ($PdCl_2(dppf)/KOAc$) using dimethyl sulfoxide (DMSO) or dioxane as solvent for 18 or 96 hr at 80 °C. An intermediate reaction time (30 h) using a mixture of the solvents gave a small amount (9 % yield) of the desired boronic ester **24** after chromatographic purification. The isolated ester, however, on a single attempt, did not couple with bromoterpyridine **15** under the "standard" Suzuki conditions ($Pd(PPh_3)_4$, toluene, ethanol, aq Na_2CO_3 , reflux).

Borylation of **15** to **7** and Subsequent Attempts to Cross-Couple with **10**

Terpyridine **15**, on the other hand, was cleanly borylated to boronic ester **7** in respectable yield by the method of Aspley and Williams.^{47c} Although unprotected 4-bromosalicylaldehydes are known to cross-couple under Suzuki conditions, reaction of **7** with **10** under the standard Suzuki conditions described above failed to give the desired hetero-coupled product **5b** in appreciable yield. In one attempted coupling, the ¹HNMR

analysis (see Appendix D) of the crude reaction mixture suggested that the desired coupled product **5b** might be present in as much as 15% yield. This was indicated by the appearance of a new aldehydic proton at 10.24 ppm; the corresponding protons in the starting phenol **10** are observed at 10.18 ppm in DMSO-d₆. In many instances, halophenols have, however, been protected before submission to Suzuki coupling conditions. In an attempt to improve the efficiency of the coupling, it was decided that it would be prudent to introduce a base-stable group to protect the phenol functionality of compound **10**.

Protection of **10** and Attempts to Cross-Couple with **7**

4-Bromo-2,6-diformylphenol **10** proved quite resistant to the introduction of several protecting groups. Reaction with dihydropyran under conditions reported⁵³ to convert phenolic substrates possessing aldehyde groups to their tetrahydropyranyl (THP) ethers did not give the THP-protected **17**. Treatment of **17** with excess *tert*-butyldimethylsilyl chloride (TBDMSCl) did not give its TBDMS ether under a variety of reaction conditions. Remarkably, every attempted reaction to methylate **10** with either dimethyl sulfate or methyl iodide gave very poor results. Several combinations of different bases, solvents, and temperature ranges were used in the attempts to form the methyl ether of **10**.

Acetate-protected 4-bromophenols have been reported to undergo Suzuki couplings using aqueous base with retention of the acetate group.⁵⁴ Acetylation of **10** with acetyl chloride in dichloromethane was problematic, but the reaction proceeded smoothly in essentially quantitative yield using THF as the solvent. Under the standard

Suzuki conditions that were employed ($\text{Pd}(\text{PPh}_3)_4$, toluene, ethanol, aq metal carbonate, 80 °C), little or no coupling was observed of the acetate-protected **10** with borylated terpyridine **7**; the acetate group appeared to have been almost completely removed as judged by ^1H NMR analysis of the crude residue obtained.

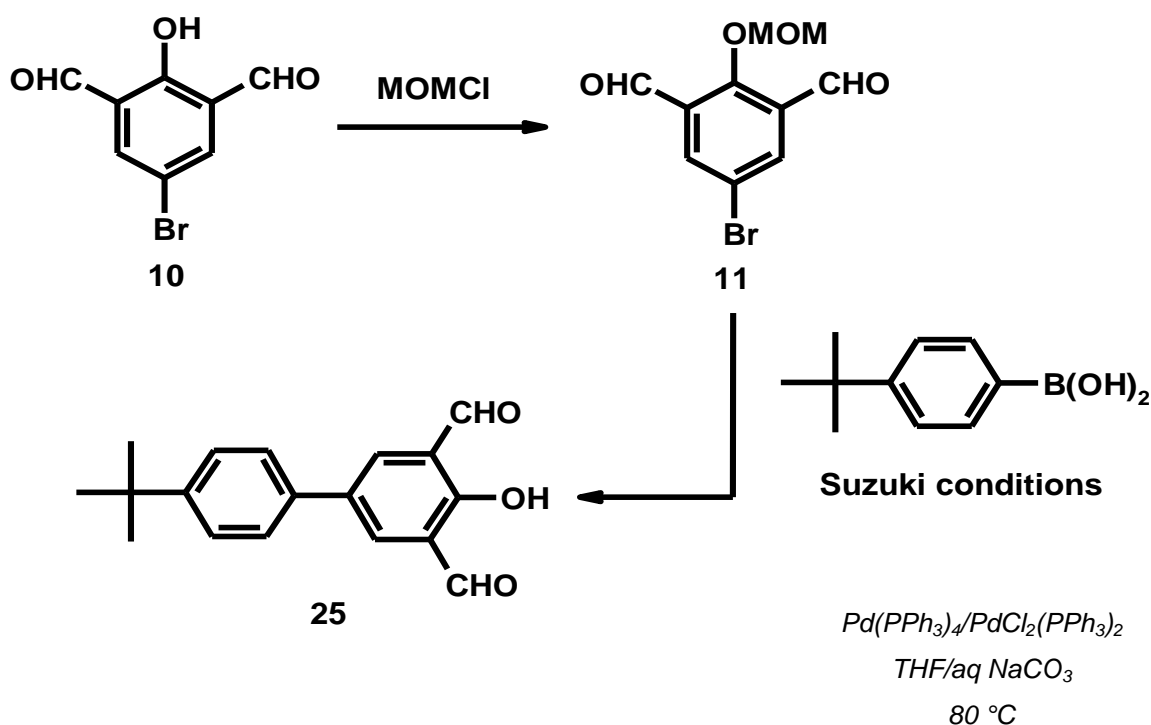
Up to this point, the use of the toxic chloromethyl methyl ether (MOMCl) to form the methoxymethyl (MOM) ether of **10** had been avoided. Use of this reagent, however, led to the smooth formation of 5-bromo-2-(methoxymethoxy)benzene-1,3-dicarbaldehyde **11**. In most preparations of **11**, the isolated yield was acceptable (ca. 75%) and was comparable to the yield reported by Ward and co-workers.⁵⁵ These workers used the MOM ether to successfully protect **10**; it was encouraging that they had also ethynylated **11** *via* the Pd(0) catalyzed Sonagashira reaction in moderate yield. It was believed that the successful Sonagashira coupling might be indicative of successful Miyaura borylation of **11** and Suzuki cross-coupling of **11** with bromo-functionalized terpyridine **15**.

Cross-Coupling of **11** with 4-*tert*-Butylphenylboronic Acid

On a first attempt, borylation of **11** did not proceed in appreciable yield using a DMSO/dioxane solvent system. MOM-protected adduct **11**, however, was quite successfully cross-coupled with 4-*tert*-butylphenylboronic acid to give diformylphenol **25** (Scheme 7) under certain conditions. The successful Suzuki coupling proceeded at 80° C and employed a THF/water solvent system. When the same reaction conditions, *i.e.*, THF/water at 80° C, were employed with **10** as the brominated partner, no appreciable heterocoupling was observed with 4-*tert*-butylphenylboronic acid. When the "standard"

reaction conditions, *i.e.*, toluene/ethanol/water at 80° C, were used with **11** as the brominated partner, again, no appreciable heterocoupling was observed with 4-*tert*-butylphenylboronic acid. Based solely on these three experiments, it appears that both protection of the phenol functionality and solvent system choice are important factors in successful Suzuki reactions with this 2,6-diformylphenol substrate.

Scheme 7. Synthesis 4'-*tert*-butyl-4-hydroxybiphenyl-3,5-dicarbaldehyde **25**.

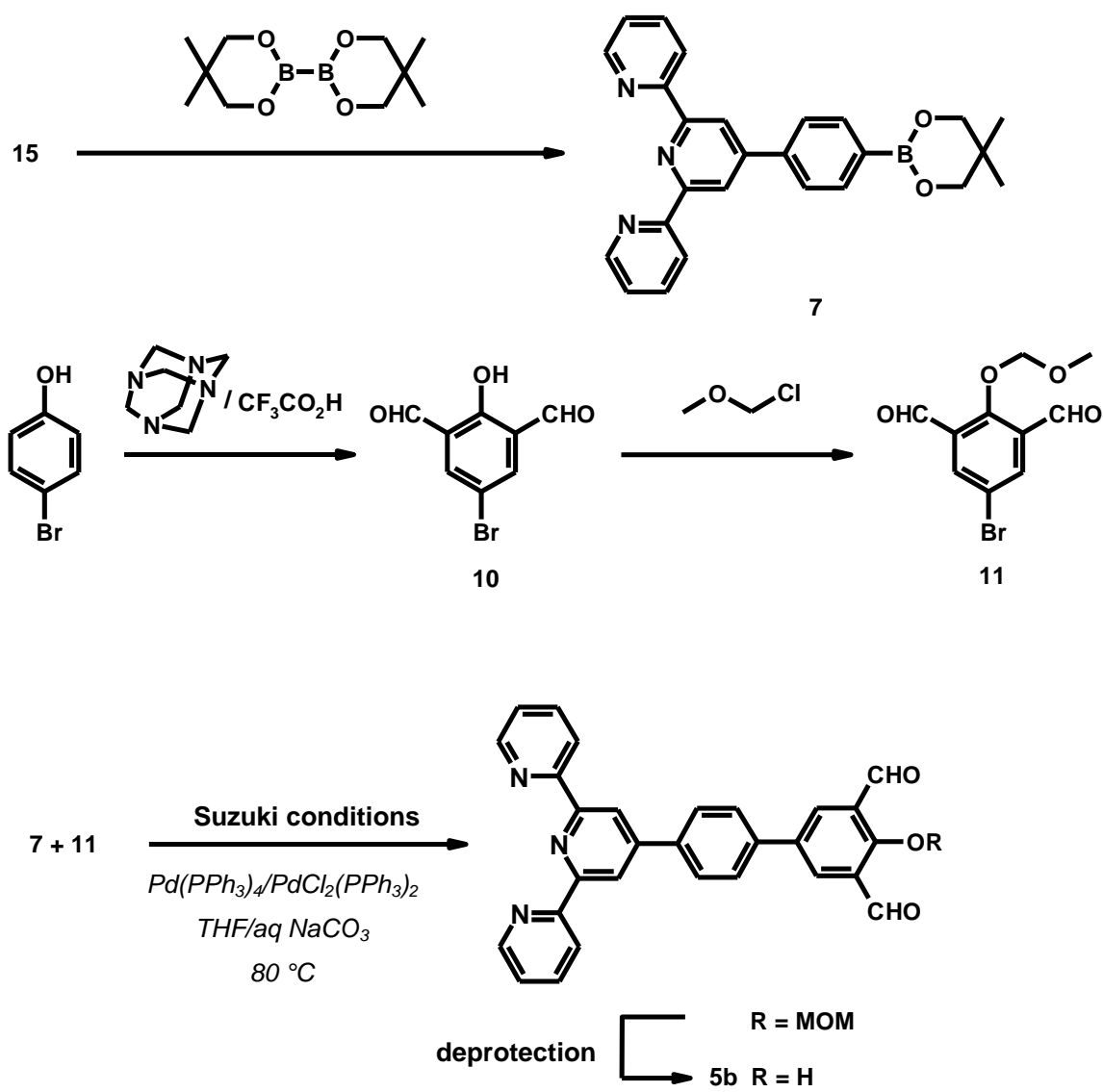


Suzuki Coupling of **11** with **7** to Give **5b**

Attempts to cross-couple boronic ester-functionalized terpyridine **7** with either 4-bromo-2,6-diformylphenol **10** or the MOM-protected version **11** had been largely unsuccessful when a toluene/ethanol/water solvent system was employed. When the THF/water solvent system described above was used, terpyridine-functionalized dialdehydes were obtained as the major products from the Suzuki reaction of **11** and **7**

(Scheme 8). The crude reaction mixture could not be separated by chromatographic purification using either alumina or silica with various eluent systems; however, analysis by ^1H NMR and ESIMS (see Appendix D) suggested that the crude product, after aqueous work-up, comprised largely desired **5b** and its MOM-protected adduct as illustrated in Scheme 8.

Scheme 8. Synthetic route to terpyridine-functionalized dialdehyde **5b**.



Attempted Preparation of Ruthenium Complex **6b** from **5b**

The crude **5b** obtained above was treated with $(\text{CH}_3\text{-}\phi\text{-tpy})\text{RuCl}_3$ (**4**) in the presence of *N*-ethylmorpholine (NEM) in ethanol (reflux, 4h) to obtain a red residue. The crude product was subjected to anion exchange conditions with aq NH_4PF_6 . The resulting red residue was analyzed by ^1H NMR and ESIMS (see Appendix D). The product was an obvious mixture by NMR and appeared, for the most part, to lack the expected aromatic aldehyde functionality. No signal corresponding to the desired complex **6b** was observed by ESIMS. It is unclear at this time as to why the attempted complexation of crude **5b** with $(\text{CH}_3\text{-}\phi\text{-tpy})\text{RuCl}_3$ proceeded without any identifiable **6b**. The only readily identified species by ESIMS were $[(\text{CH}_3\text{-}\phi\text{-tpy})\text{Ru}(\text{tpy-Ph})]^{2+}$ and its PF_6^- adduct along with some apparently oligomeric species that did not contain ruthenium. Ph-tpy **16** was observed as a contaminant in the coupling reaction to form **5b**; however, the desired diformylated species were by far the major products of that reaction. Chakrovorty and co-workers showed that decarbonylation of 2,6-diformyl-4-methylphenol occurred in the presence of ruthenium(II) to give the *ortho*-metallated phenolate.⁵⁶ They confirmed that the reaction proceeded in near-quantity in the presence of a primary amine after briefly heating in ethanol. Although there was no primary amine in the attempted complexation reaction, perhaps the presence of NEM catalyzed the decarbonylative metallation by a related route. Other complexation protocols that do not rely on NEM as a reductant, such as the one shown in Schemes 1 and 2 and described elsewhere,^{47c} might prove more reliable for the formation of **6b** from **5b** and **4**. It is also possible that the presence of oligomeric species in the ESIMS spectrum might indicate

self- or other condensation reactions of diformylphenol **5b**, although no reasonable structure has yet been postulated; the presumed oligomeric species differ by 74 m/z units.

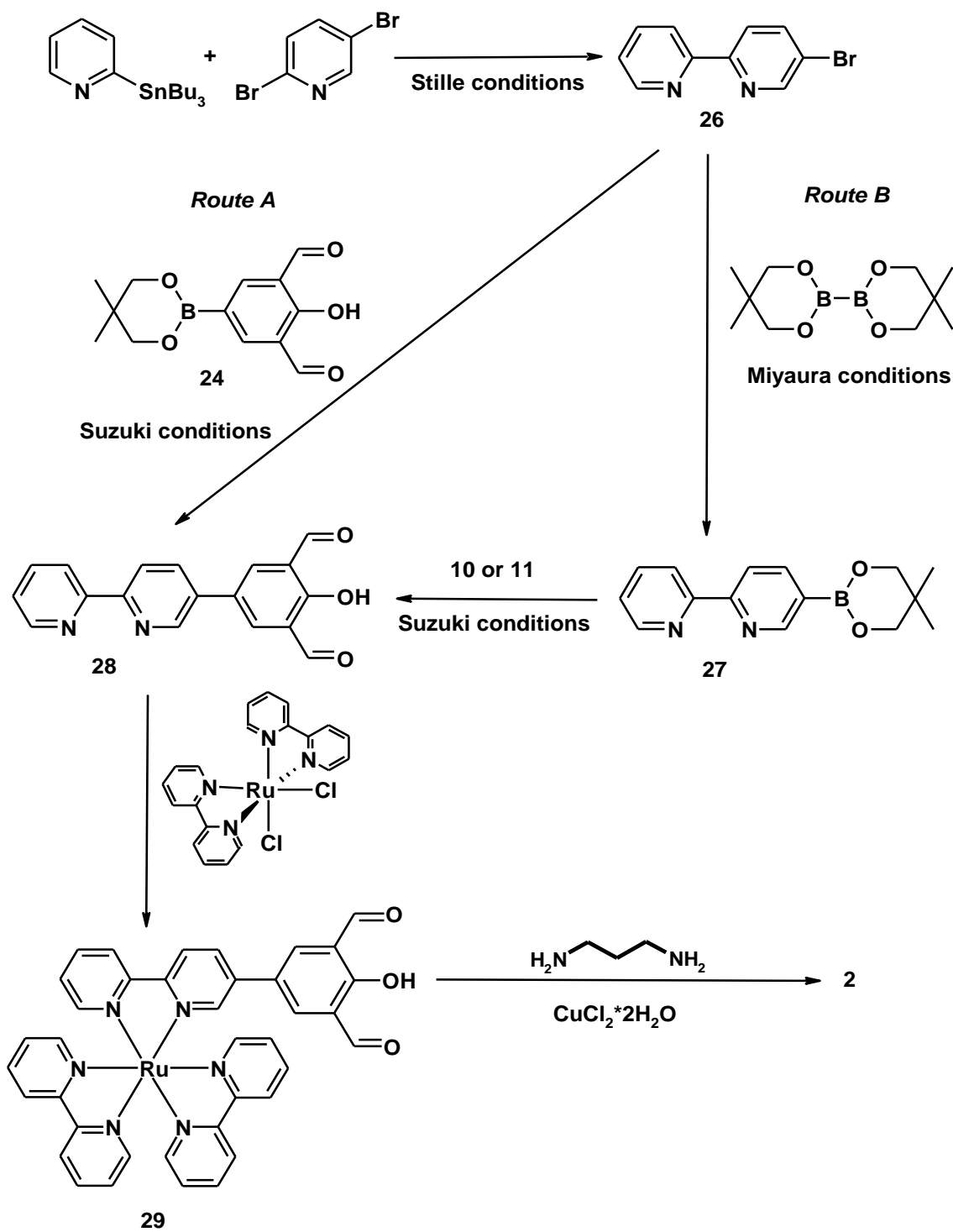
Towards Preparation of Triads 2

Synthetic routes to triad **2** are shown in Scheme 9. In these proposed pathways, the synthesis of supramolecular complex **2** depended on either the cross-coupling of 5-bromo-2,2'-bipyridine **26** with dialdehyde **24** (route A) or cross-coupling of **11** or **25** with the unknown boronic acid-functionalized bipyridine **27** (route B) to give the 2,6-diformylphenol-functionalized bipyridine **28**. Compound **26** was synthesized by the Pd(0) catalyzed Stille coupling of 2-tributylstannylpyridine with 2,5-dibromopyridine in refluxing xylenes in moderate yield by slight modifications of reported procedures.⁵⁷

Compound **26** was treated with B₂(neo)₂ in dioxane in the presence of KOAc and PdCl₂(dppf) at 80 °C. After 12 h reaction time and subsequent work-up, the desired boronic ester **27** was not readily observed in the reaction mixture. Analysis by ¹HNMR indicated that the reaction residue appeared to comprise largely unchanged starting materials.

Also, a single attempt to couple **26** and **24** under "standard" Suzuki conditions (toluene/ethanol/aq NaCO₃, Pd(PPh₃)₄, 80 °C) did not yield the desired bipyridine-functionalized diformylphenol **28** in appreciable quantity as evidenced by ¹HNR analysis of the obtained crude reaction product. It is possible that changing the solvent system from toluene/ethanol to THF or some other ether, such as dimethoxyethane, would improve the efficiency of this reaction as was found for the terpyridine systems.

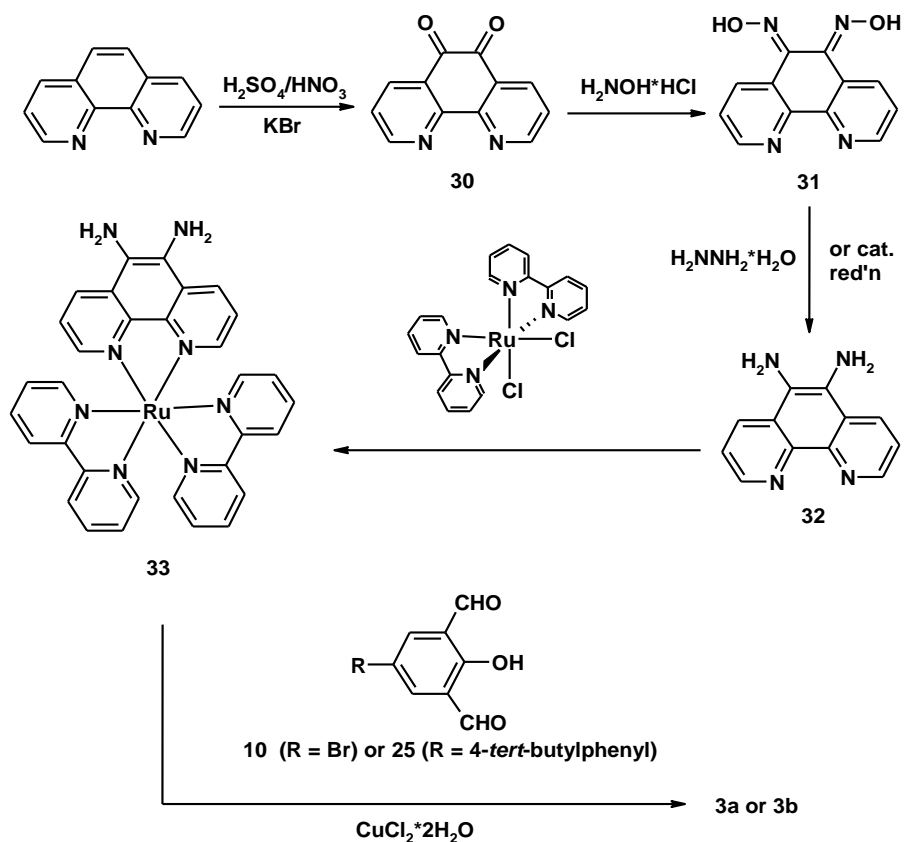
Scheme 9. Proposed synthetic routes to targeted supramolecular triad **[2]**⁶⁺. Counteranions and charges on the complexes are omitted to simplify the graphic.



Towards Preparation of Triads 3

A proposed route to triads **3** is shown in Scheme 10. Work towards complexes **3** was limited. As noted above, compound **25** was successfully prepared *via* the Suzuki reaction. 1,10-Phenanthroline was oxidized with $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{KBr}$ to give 1,10-phenanthroline-5,6-dione **30** (phendione). The phendione obtained was further reacted with hydroxylamine hydrochloride in ethanol in the presence of sodium carbonate to give 1,10-phenanthroline-5,6-dioxime **31**. The syntheses of both of these two compounds were based on well established procedures and rendered the desired compounds in close to the reported yields.⁵⁸

Scheme 10. Proposed synthetic route to targeted supramolecular triads [**3**]⁶⁺. Counteranions and charges on the complexes are omitted to simplify the graphic.



CHAPTER 3

CONCLUSIONS AND RECOMMENDATIONS

Significant progress toward the construction of the tetranuclear bimetallic triad **1b** was realized. Specifically, a procedure was developed whereby MOM-protected 4-bromo-2,6-diformylphenol **11** was efficiently and cleanly cross-coupled with 4-*tert*-butylphenylboronic acid. This is the first reported Suzuki coupling of compound **11** to give a 4-aryl-2,6-diformylphenol. Furthermore, **11** was cross-coupled with terpyridine-functionalized boronic ester **7** to give **5b**, a key intermediate in the synthesis of complex **1b**. This is the first reported synthesis of a terpyridine-functionalized 2,6-diformylphenol.

The cross-coupling of **10** with **7** to give terpyridine-functionalized diformylphenol **5b** was an unoptimized reaction. Some Suzuki couplings are often very sensitive to the nature of the solvent, as was demonstrated in the coupling of MOM-protected 4-bromo-2,6-diformylphenol **11** with 4-*tert*-butylphenylboronic acid. Dimethoxyethane (DME) has been shown to be among the best solvents for Suzuki reactions where terpyridine moieties were the coupling partner(s).⁴⁷ Its use as solvent should be investigated in this system.

Other coupling reactions should also be investigated. For example the Stille or Negishi reactions might prove more robust for substrates of these types.

It is also recommended that the use of acetylenic linking groups be investigated. Literature precedent exists⁵⁵ for the ethynylation of compound **11** *via* the Sonagashira reaction. There are also many reported references of using acetylenes or catenated acetylenes to link polypyridyl moieties to other groups including metal complexes.⁵⁹

CHAPTER 4

EXPERIMENTAL

Physical Measurements

UV-visible absorption spectra were recorded on a Shimadzu UV-2401PC UV- vis recording spectrophotometer.

Analyses for C, H, and N were processed on a ThermoFinnigan FlashEA 1112 series elemental analyzer.

¹HNMR spectra were recorded at ambient temperature using a Varian Mercury 300 MHz spectrometer; chemical shifts were measured relative to the solvent reference (dimethyl sulfoxide-d₆: 2.49 ppm; chloroform-d: 7.27 ppm; acetonitrile-d₃: 1.94 ppm).

Mass spectral analyses were conducted using positive ion electrospray mass spectrometry employing a Waters LCT-TOF (time-of-flight) mass spectrometer. The resolution of the mass spectrometer is approximately 5000 at peak half height. In the case of copper complex **12**, the sample was dissolved in water (1 mg in 1.5 mL) and then diluted (20 μL of the solution into 1.5 mL of water). The samples were infused into the mass spectrometer with a Hamilton syringe pump at 10 μL/minute with a source cone voltage of 20 volts.

The instrument was calibrated with a solution of polypropylene glycol (average MW 1000) in a mixture of 50/50 volume/volume water/acetonitrile containing 4 mmolar ammonium acetate. The source cone voltage was set at 50 volts to give a mixture of (M+NH)⁺ ions and fragment ions.

Materials

All commercially available materials were used without any further purification and were obtained from Aldrich, TCI America, Frontier Scientific, Alfa Aesar, Mallinckrodt, VWR, Burdick and Jackson, J.T. Baker, or Eastman Chemical Company. Solvents were reagent grade or better. The dry trifluoroacetic acid (TFA) used in the modified Duff reactions was either redistillation, for protein sequencing or spectrophotometric grade from Aldrich. Reagent grade TFA, either from Aldrich or Mallinckrodt, did not afford the desired transformation in these reactions, presumably due to its higher water content.

Preparations

Synthesis of Selected Mono-Terpyridine Compounds

4'-(4-Hydroxyphenyl)-2,2':6',2''-terpyridine (tpy- ϕ -OH) (14). 2-Acetylpyridine (23.23 g, 192 mmol) was added to a solution of 4-hydroxybenzaldehyde (mmol) in ethanol (480 mL). KOH pellets (14.8 g, 85%, 192 mmol) and conc aq NH₃ (280 mL, 28-30%, ca. 240 mmol) were added to the solution. After the KOH had dissolved (less than 2 min) the reaction vessel was loosely capped and the solution was allowed to stand for 1 week at room temperature. The potassium salt of the desired compound, which precipitated as a dark yellow powder, was collected by filtration. Additional free phenol could be obtained as tan flakes by neutralization of the filtrate with HOAc. (combined yield: 30%).

4'-(4-Bromophenyl)-2,2':6',2''-terpyridine (tpy- ϕ -Br) (15). 2-Acetylpyridine (23.23 g, 192 mmol) was added to a solution of 4-bromobenzaldehyde (96 mmol) in ethanol (480 mL). KOH pellets (14.8 g, 85%, 192 mmol) and conc aq NH₃ (280 mL, 28-30%, ca. 240 mmol) were added to the solution. After the KOH had dissolved, the reaction vessel was loosely capped and the solution was allowed to stand overnight. The desired compound was collected as an off-white powder by filtration. The powder was washed with cold ethanol and air dried (yield: 17.2 g, 46%).

4'-(Phenyl)-2,2':6',2''-terpyridine (tpy-Ph) (16). 2-Acetylpyridine (23.23 g, 192 mmol) was added to a solution of benzaldehyde (96 mmol) in ethanol (480 mL). KOH pellets (14.8 g, 85%, 192 mmol) and conc aq NH₃ (280 mL, 28-30%, ca. 240 mmol) were added to the solution. After the KOH had dissolved, the reaction vessel was loosely capped and the solution was allowed to stand overnight. The desired compound was collected as an off-white powder by filtration. The powder was washed with cold ethanol and air dried (yield: 29.7g, 20%).

4'-(4-Methylphenyl)-2,2':6',2''-terpyridine (tpy- ϕ -CH₃) (17). 2-Acetylpyridine (23.23 g, 192 mmol) was added to a solution of *p*-tolualdehyde (96 mmol) in ethanol (480 mL). KOH pellets (14.8 g, 85%, 192 mmol) and conc aq NH₃ (280 mL, 28-30%, ca. 240 mmol) were added to the solution. After the KOH had dissolved, the reaction vessel was loosely capped and the solution was allowed to stand overnight. The desired compound was collected as off-white needles by filtration. The needles were washed with cold ethanol and air dried (yield: 9.1 g, 29%).

4'-(4-Methoxyphenyl)-2,2':6',2''-terpyridine (tpy- ϕ -OMe) (18). 2-Acetylpyridine (23.23 g, 192 mmol) was added to a solution of 4-bromobenzaldehyde (96 mmol) in ethanol (480 mL). KOH pellets (14.8 g, 85%, 192 mmol) and conc aq NH₃ (280 mL, 28-30%, ca. 240 mmol) were added to the solution. After the KOH had dissolved, the reaction vessel was loosely capped and the solution was allowed to stand overnight. The desired compound was collected as an off-white powder by filtration. The powder was washed with cold ethanol and air dried (yield: 3.9 g, 12%).

4'-(4-Acetamidophenyl)-2,2':6',2''-terpyridine (tpy- ϕ -NHAc) (19). 2-Acetylpyridine (23.23 g, 192 mmol) was added to a solution of 4-acetamidobenzaldehyde (96 mmol) in ethanol (480 mL). KOH pellets (14.8 g, 85%, 192 mmol) and conc aq NH₃ (280 mL, 28-30%, ca. 240 mmol) were added to the solution. After the KOH had dissolved, the reaction vessel was loosely capped and the solution was allowed to stand overnight. The desired compound was collected as off-white needles by filtration. The powder was washed with cold ethanol and air dried (yield: 14.1 g, 40%).

4'-(4-Hydroxy-3,5-dibromophenyl)-2,2':6',2''-terpyridine (20) 2-Acetylpyridine (23.23 g, 192 mmol) was added to a hot solution of 4-hydroxy-3,5-dibromobenzaldehyde (96 mmol) in ethanol (480 mL). KOH pellets (14.8 g, 85%, 192 mmol) and conc aq NH₃ (280 mL, 28-30%, ca. 240 mmol) were added to the solution. ¹H NMR analysis showed that the solid that had deposited after 15 h was largely the intermediate aza-chalcone, or its potassium salt. The mixture was heated at reflux for 8 h. After cooling, the potassium

salt of the desired compound was collected by filtration as bright orange flakes (yield: 7.5 g, 15%).

4'-(4-Methoxy-3,5-dibromophenyl)-2,2':6',2''-terpyridine (21) The potassium salt of 4'-(4-Hydroxy-3,5-dibromophenyl)-2,2':6',2''-terpyridine (4.0 g, 7.6 mmol) was slurried with K₂CO₃ in acetone (50 mL) and DMSO (50 mL). An excess of methyl iodide (6 g) was added and the mixture was warmed to ca. 60 °C for 15 min during which time the orange color discharged completely and a white microcrystalline precipitate deposited. The acetone and excess methyl iodide were removed by rotary evaporation. The residue was diluted with warm water and the product was isolated by filtration and subsequently washed with more warm water. The wet cake was reslurried in boiling acetone. After cooling, the desired compound was collected by filtration as an almost colorless microcrystalline powder in near quantitative yield.

Synthesis of Brominated Dialdehydes

4-Bromo-2,6-diformylphenol (10). 4-Bromophenol (50.8g) and hexamethylenetetramine (83.8 g) were added to dry trifluoroacetic acid (TFA, 375 mL). The solution was heated at reflux (140 °C external temperature) for 3 d then poured hot into 4 N HCl (1200 mL). After standing 15 h, a bright yellow precipitate separated and was removed by filtration. Recrystallization from ethanol/water gave short pale yellow needles (20%). In most preparations of this compound, the crude product was sufficiently pure, as judged by ¹H NMR, to be used in subsequent reactions. The isolated yield of purified product could be improved from 20% to ca. 60% if purified by

chromatography (silica, EtOAc/heptane, gradient 15–40 v %) rather than recrystallization. In some preparations of this compound, unexplainably, a very large amount (ca. 60 wt %) of $\text{CF}_3\text{C}(\text{O})\text{NHCH}_2\text{NHC}(\text{O})\text{CF}_3$ coprecipitated with the desired crude product from acid solution. In those cases, it was found that the undesirable bis-amide could not be efficiently removed by chromatography using the EtOAc/heptane system, but it was quite insoluble in chloroform and could be removed by simple filtration. The filtrate was then slurried with silica, filtered again, and evaporated to leave **17** in ca. 43% yield.

5-Bromo-2-(methoxymethoxy)benzene-1,3-dicarbaldehyde (11). To a solution of 4-bromo-2,6-diformylphenol **10** (22 g) in DMF (250 mL) was added anhydrous K_2CO_3 (64 g). The solution was cooled in an ice bath and neat chloromethylmethylether (12 g) was added dropwise *via* syringe. The mixture was stirred 16 h at RT, then water (300 mL) was added. The resulting precipitate was collected by filtration and washed with water. After drying on the filter overnight, TLC analysis (silica, 50/50:EtOAc/heptane) of the yellow-beige powder showed that the crude product comprised primarily a single species although some baseline impurities were noted. The starting diformylphenol was absent from the crude product. The powder was dissolved in EtOAc (50 mL) and silica (40 g) was added. The mixture was stirred briefly then diluted with heptane (150 mL). The mixture was poured onto a short plug of silica and eluted with additional EtOAc/heptane (600 mL, 1/3:v/v). The solvent was removed to leave a colorless crystalline residue. Analysis by TLC showed the same compound, but without any baseline impurities (yield: 20 g, 76%).

Pd(0) Catalyzed Reactions

2,6-Diformyl-4-(neopentyl glycolatoboron)phenol (24). Under a gentle flow of dry argon, to a Schlenk flask containing dialdehyde **10** (3.64 mg, 15.9 mmol), bis(neopentyl glycolato)diboron (3.77 g, mmol), KOAc (4.69 g, mmol), and PdCl₂(dppf) (300 mg), were added anhydrous deaerated DMSO (80 mL) and anhydrous deaerated dioxane (80 mL). Argon was bubbled through the mixture for 40 min at RT. The flask was heated at 80 °C under argon for 30 h. After cooling, the reaction mixture was diluted with toluene and washed with water. The organic extracts were dried over MgSO₄ and concentrated by rotary evaporation. The residue was chromatographed over silica (EtOAc/heptane) and the desired product was isolated as a pale cream-colored solid (yield; 375 mg, 9%).

4'-(4-Neopentyl glycolatoboronphenyl)-2,2':6',2''-terpyridine (tpy- ϕ -Bneo) (7).

Similar to the literature^{47c} procedure: Under a gentle flow of dry nitrogen, a Schlenk flask was charged with bis(neopentyl glycolato)diboron (2.85 g, 12.6 mmol), KOAc (3.53 g, 36 mmol), PdCl₂(dppf) (300 mg), terpyridine **9** (4.66 g, 12 mmol), and anhydrous deaerated DMSO (120 mL). Nitrogen was bubbled through the mixture for 40 min at RT. The flask was heated at 80 °C under nitrogen for 10 h. After cooling, the reaction mixture was diluted with toluene (800 mL) and washed with water (4 × 1 L). The organic extracts were dried over MgSO₄ and concentrated by rotary evaporation to give the product as an off-white solid (yield: 3.4 g, 67%).

4'-tert-butyl-4-hydroxybiphenyl-3,5-dicarbaldehyde (25). Protected diformylphenol **11** (819 mg, 3 mmol), 4-tert-butylphenylboronic acid (588 mg, 3.3 mmol), Na₂CO₃ (1.3

g), water (7 mL), THF (80 mL), tetrakis(triphenylphosphine)palladium(0) (90 mg), and dichlorobis(triphenylphosphine)palladium(II) (70 mg) were charged to a Schlenk flask. Nitrogen gas was bubbled through the reaction mixture for 40 min. The tube was sealed under nitrogen and heated at 80 °C for 12 h. Analysis by TLC suggested that compound **11** had been completely consumed. After cooling, the mixture was diluted with toluene and washed repeatedly with water. The organic extracts were dried over MgSO₄ and concentrated by rotary evaporation. The residue was chromatographed over silica (EtOAc/heptane). The desired product was collected as a yellow powder (yield; 439 mg, 52%). Mass spectral and ¹HNMR analysis confirmed the identity of the purified product.

4'-(3,5-Diformyl-4-hydroxyphenyl)-2,2':6',2''-terpyridine and 4'-(3,5-diformyl-4-(methoxymethoxy)phenyl)-2,2':6',2''-terpyridine (5b and its methoxymethyl ether).

Protected diformylphenol **11** (104 mg, 0.38 mmol), terpyridine **7** (160 mg, 0.38 mmol), Na₂CO₃ (162 mg,), water (0.85 mL), THF (10 mL), tetrakis(triphenylphosphine)palladium(0), (12 mg) and dichlorobis(triphenylphosphine)palladium(II) (8 mg) were charged to a Schlenk tube. Nitrogen gas was bubbled through the reaction mixture for 40 min. The tube was sealed under nitrogen and heated at 80 °C for 12 h. Analysis by TLC suggested that compound **7** had been completely consumed. After cooling, DMF was added to dissolve the hard residue. The mixture was diluted with toluene and water then neutralized by addition of acetic acid and washed repeatedly with water. The organic extracts were dried over MgSO₄ and concentrated by rotary evaporation. Analysis by ¹HNMR suggested that cross-coupling had been successful, but the protecting group had to a large extent been

removed. Mass spectral analysis confirmed that the **5b** was the major product of the reaction with a minor ion corresponding to its MOM ether (combined crude yield: 155 mg). Several other minor ions were observed in the mass spectrum of the crude reaction product.

Synthesis of Metal Complexes

[Ru(CH₃- ϕ -tpy)]Cl₃ (4). Ruthenium(III) chloride hydrate (320 mg, 12.4 mmol) and 4'-(4-methylphenyl)-2,2':6',2''-terpyridine (**17**, CH₃- ϕ -tpy, 400 mg, 12.4 mmol) were suspended in ethanol (40 mL). The suspension was heated at reflux for 10 h. After the mixture had cooled to room temperature, the red-brown solid was filtered off, washed with cold ethanol, and dried *in vacuo* (yield: 427 mg, 64%).

[Ru(CH₃- ϕ -tpy)(B(OH)₂- ϕ -tpy)](PF₆)₂ (8). Similar to the literature^{47c} procedure: Ru(tpy- ϕ -CH₃)Cl₃ (162 mg, 3.05 \times 10⁻⁴ mol) and AgBF₄ (179 mg, 9.16 \times 10⁻⁴ mol) were suspended in a mixture of acetone (128 mL) and absolute ethanol (32 mL) and were heated at 75 °C for 3 h under nitrogen. After cooling, the AgCl was removed by filtration through Celite. Ethanol (30 mL) was added and the acetone was removed by evaporation without heating. Ethanol was added to give 100 mL total volume. Compound **7** (128 mg, 3.05 \times 10⁻⁴ mol) was added and the flask was covered with aluminum foil. The solution was heated under nitrogen for 3.5 h then concentrated to dryness. The residue was dissolved in a minimum of acetonitrile then added dropwise to a saturated aqueous solution of NH₄PF₆. The red precipitate was chromatographed over silica as described in the literature.^{47c} Note that the ester is cleaved upon chromatography to give the boronic acid (yield: 146 mg, 45%).

[Cu₂(Br-M-Br)(H₂O)_x]Cl₂ (M = 4,4'-diradical of the dianion of the Robson macrocycle derived from the 2 + 2 condensation of 2,6-diformylphenol with 1,3-diaminopropane) (12). Cupric chloride dihydrate (1.11 g, 6.5 mmol) was dissolved in methanol (ca. 15 mL) to give a green solution. 1,3-Diaminopropane (0.58 g, 0.65 mL, 7.8 mmol) was added dropwise *via* syringe to give an immediate dark blue supernatant and heavy light blue precipitate. 4-Bromo-2,6-diformylphenol **10** (1.49 g, 6.5 mmol) was dissolved in boiling methanol (ca. 20 ml) then added in small portions to the copper-diamine complex. The supernatant turned green, but it was evident that the precipitate was still light blue. More methanol, to give a total volume of ca. 100 mL, was added and the mixture was refluxed in air for 16 h. The reaction mixture was filtered hot, and the green powder that was collected was washed with THF (100 mL) then dried in air (yield: 1.604 g, 64% if dihydrate). Percent C, H, and N, calculated for the cation: C, 34.48; H, 3.16; N, 7.31; found: C, 34.52; H, 2.83; N, 7.10.

[Zn₂(Br-M-Br)(H₂O)_x](BF₄)₂ (13). Zinc tetrafluoroborate hydrate (454 mg, 1.91 mmol) 1,3-diaminopropane (141 mg, 162 μ L, 1.91 mmol) and compound **10** (437 mg, 1.91 mmol), were heated at reflux in methanol (ca. 40 mL) for 4 h. Upon cooling, yellow crystals deposited from solution. The crystals were isolated by suction filtration, and were washed with a little cold methanol on the filter (yield: 425 mg, 53 %).

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APPENDICES

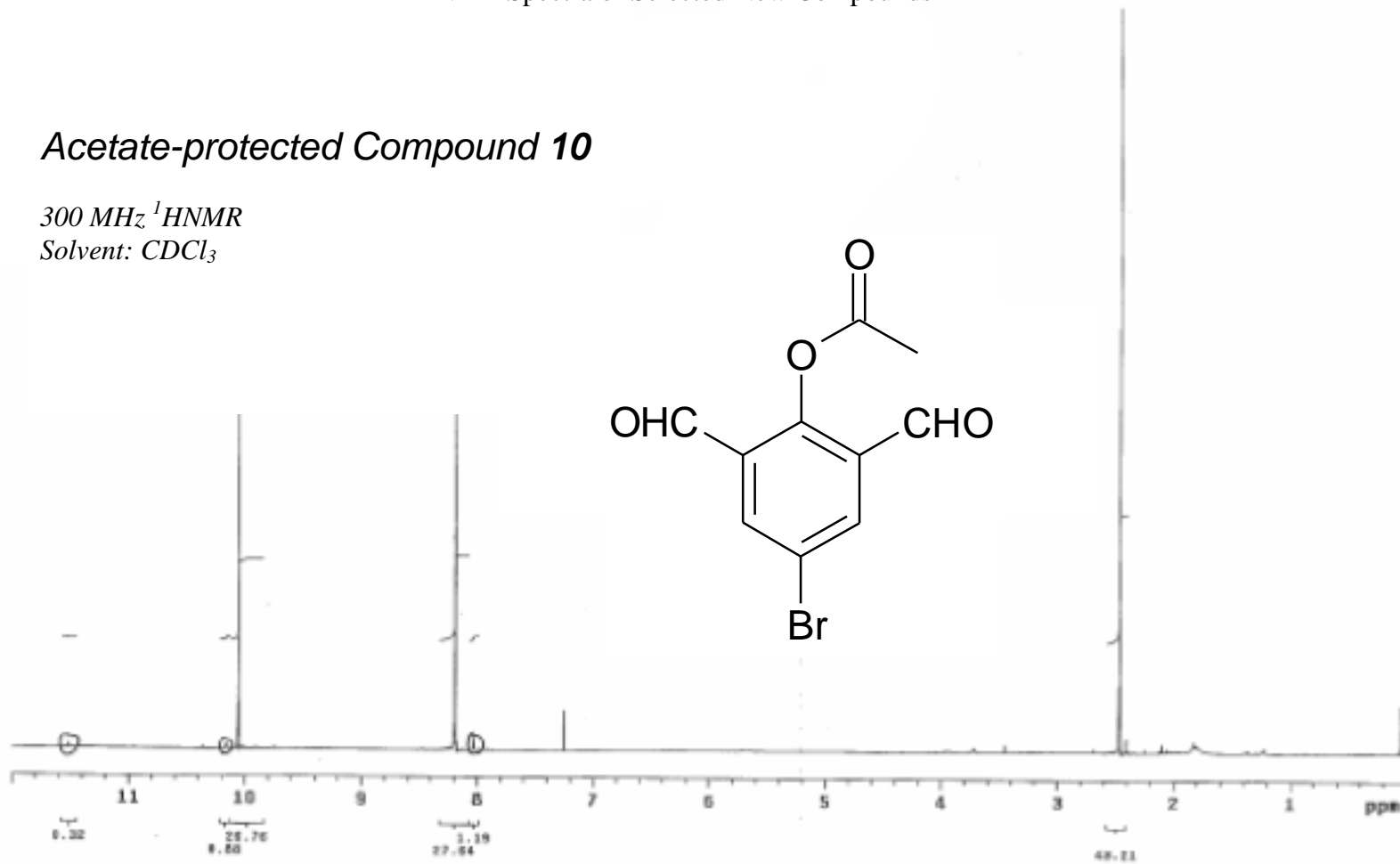
APPENDIX A

¹HNMR Spectra of Selected New Compounds

Acetate-protected Compound 10

300 MHz ¹HNMR

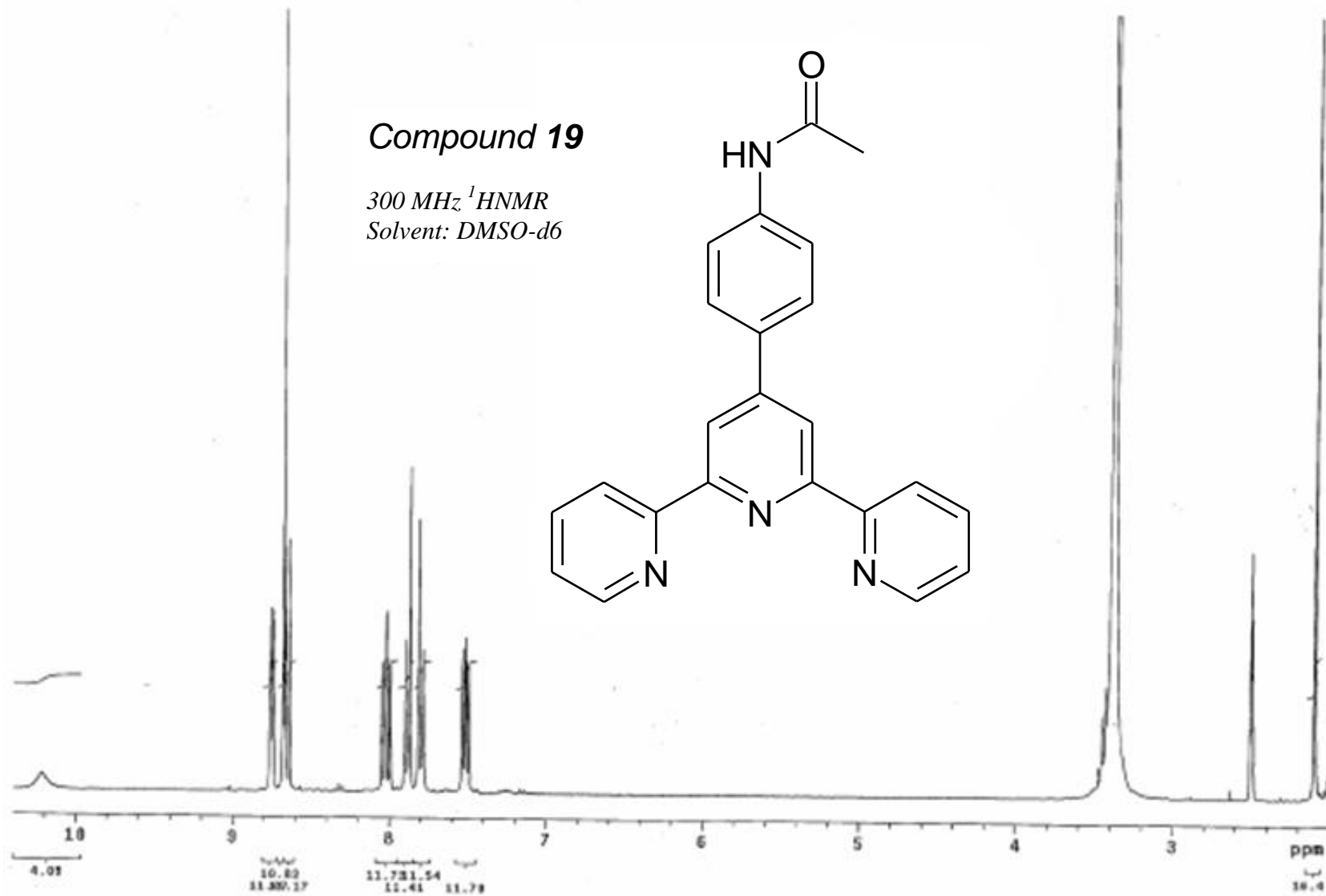
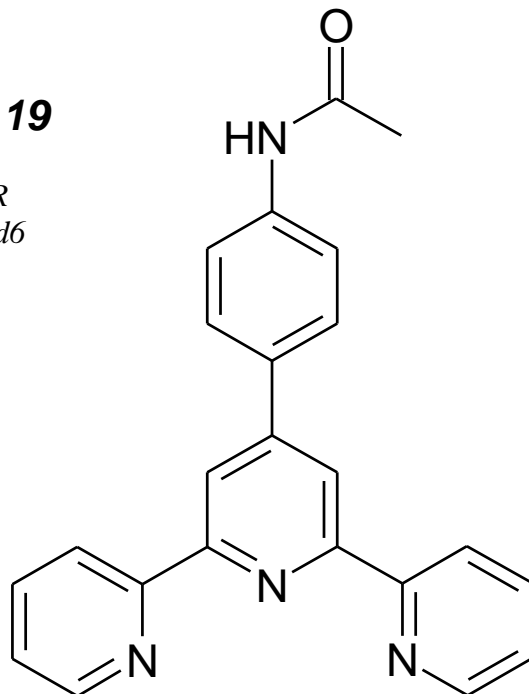
Solvent: CDCl₃



Compound 19

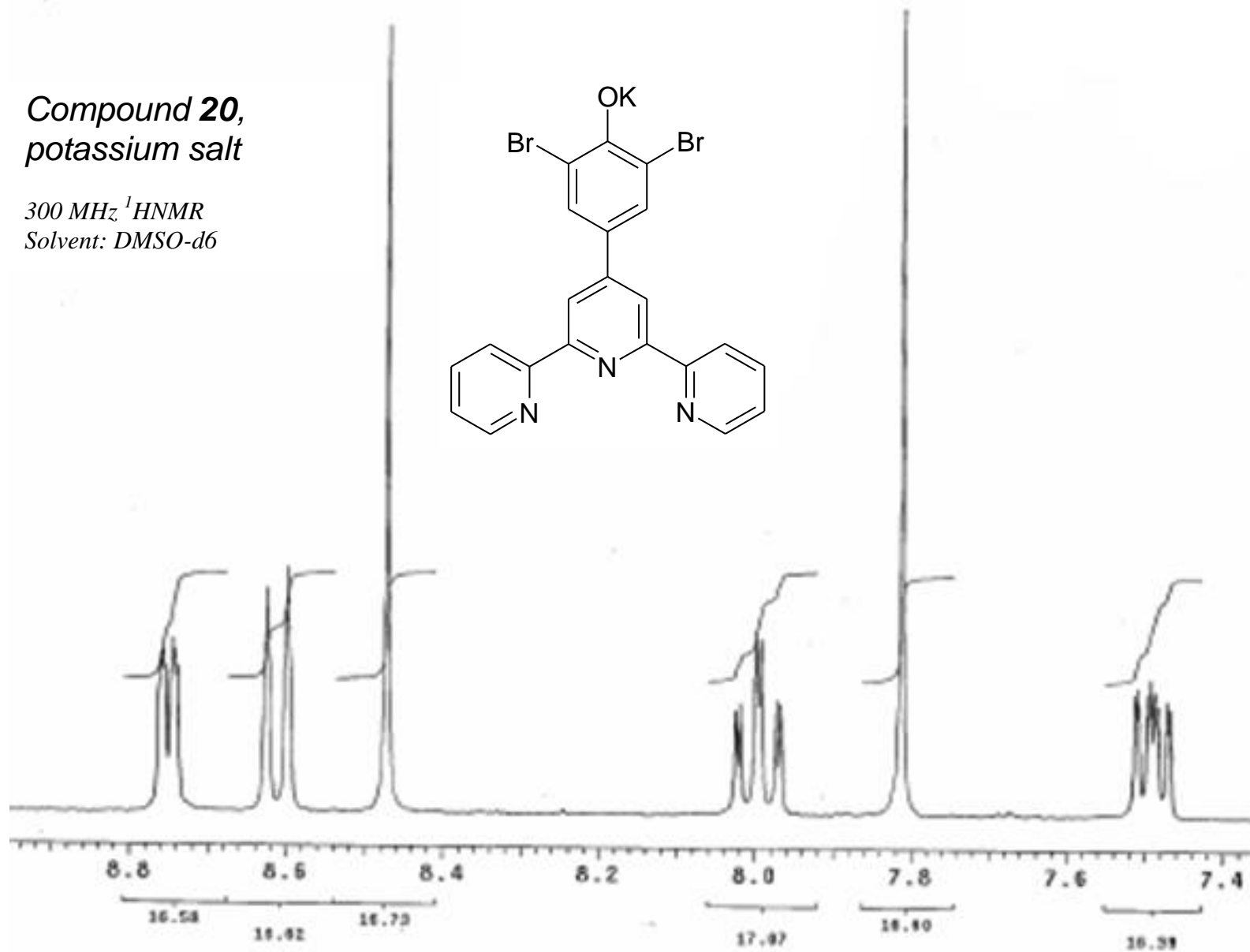
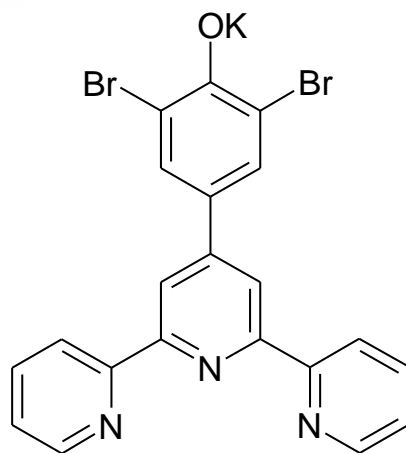
300 MHz ^1H NMR

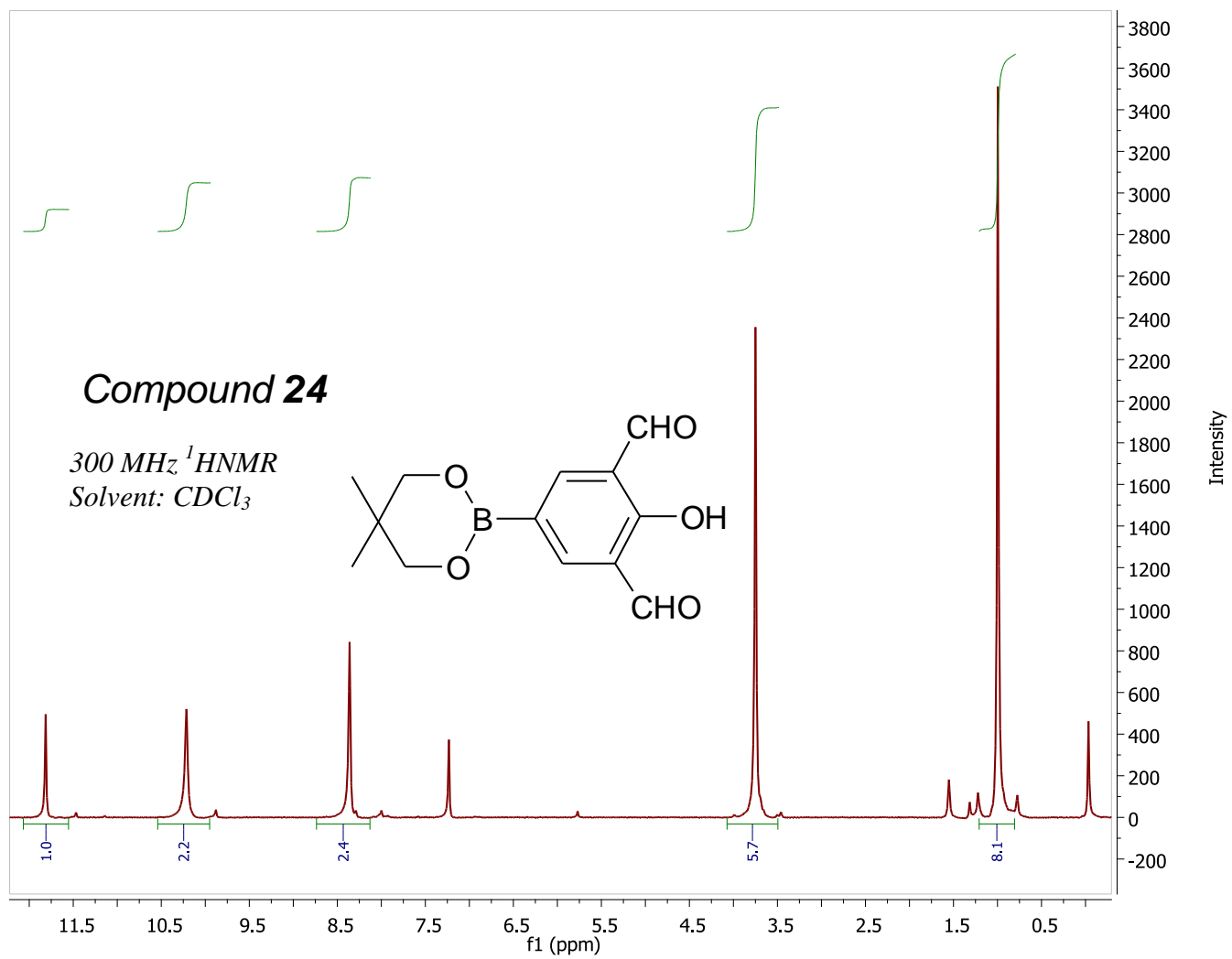
Solvent: DMSO- d_6

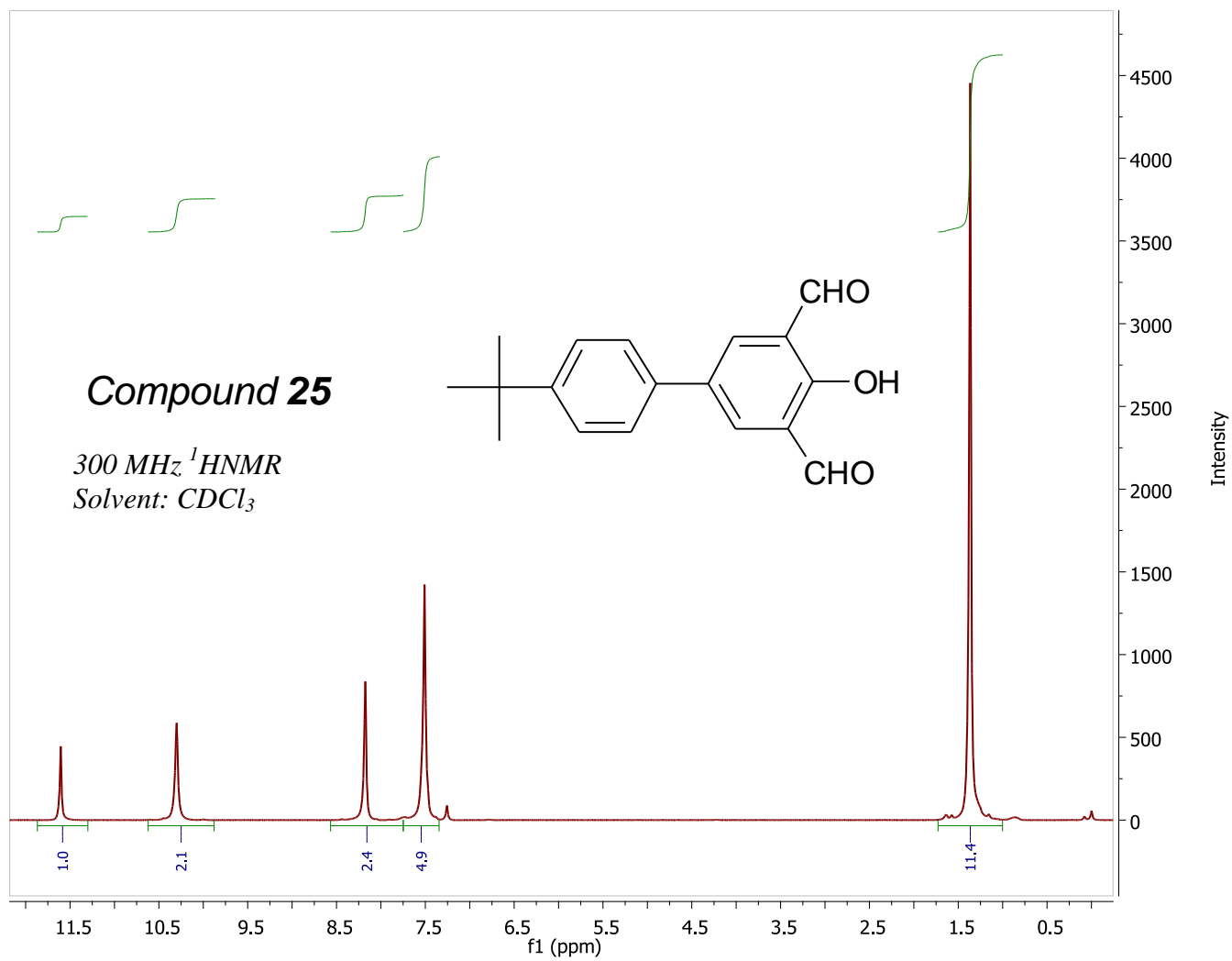


Compound 20,
potassium salt

300 MHz ^1H NMR
Solvent: DMSO- d_6



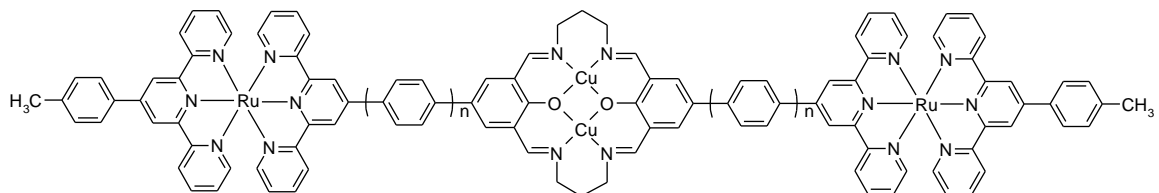




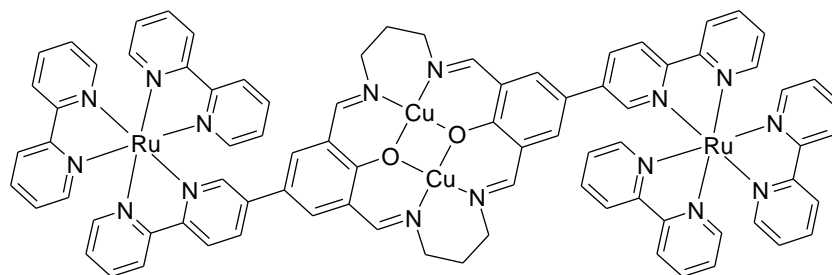
APPENDIX B:

Sequentially Numbered Chemical Structures of Synthetic Targets and Intermediate

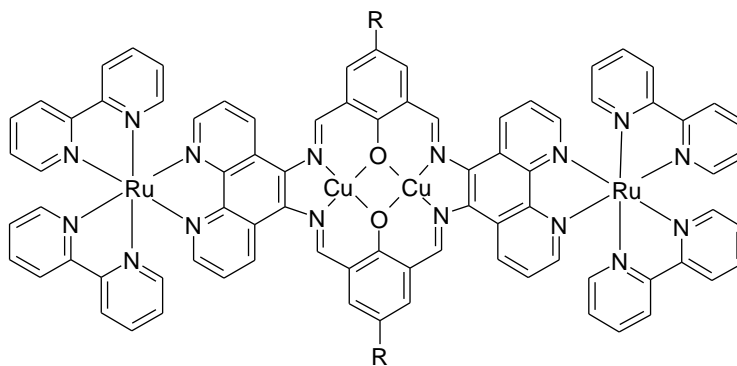
Compounds



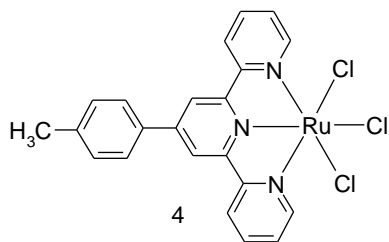
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1b n = 1



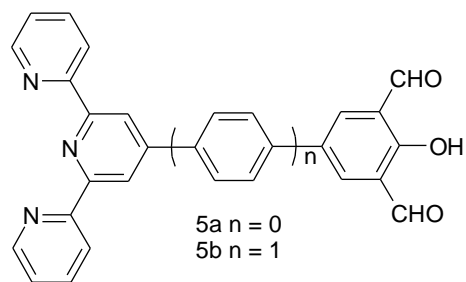
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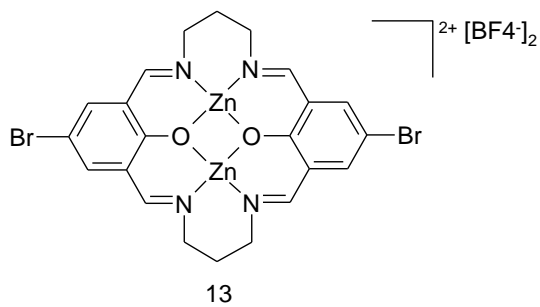
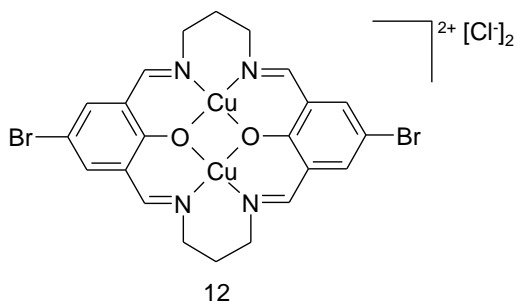
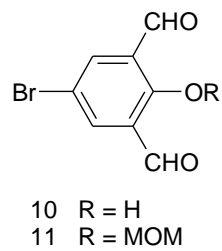
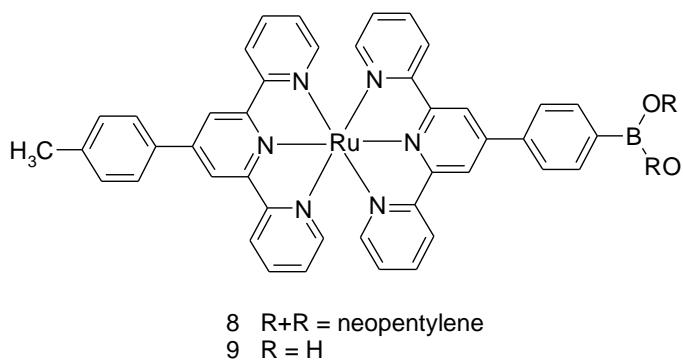
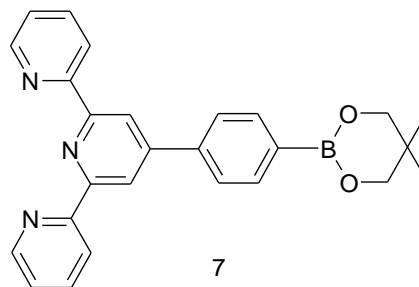
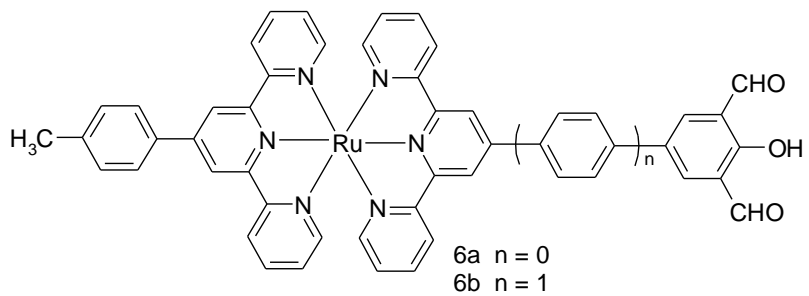
3a R = Br
3b R = 4-tert-Bu-C₆H₄

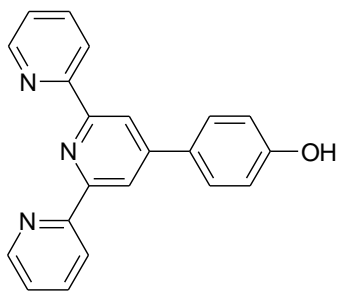


4

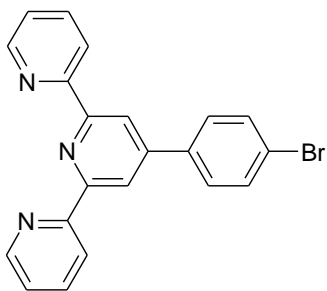


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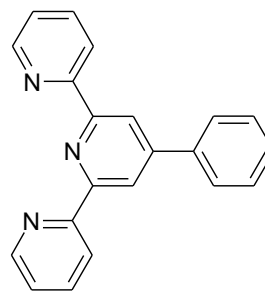




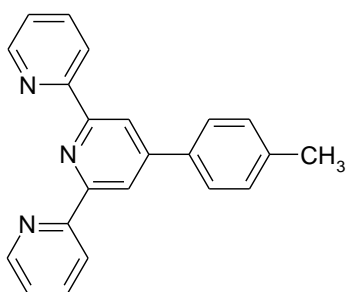
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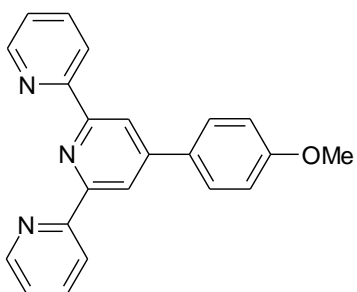
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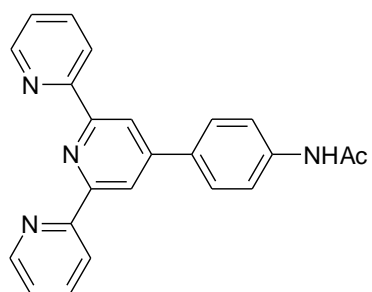
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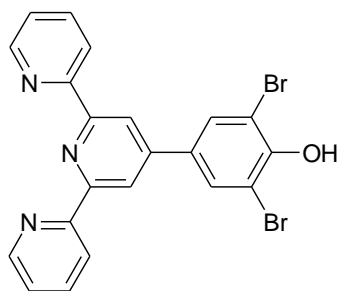
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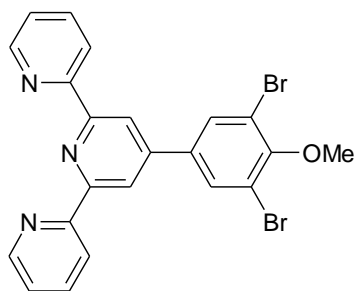
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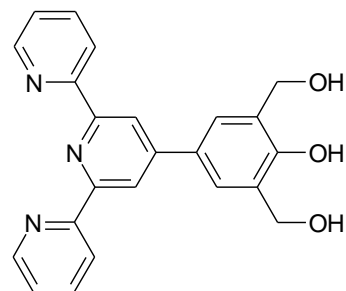
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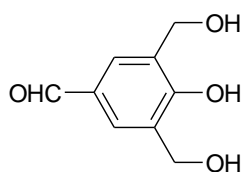
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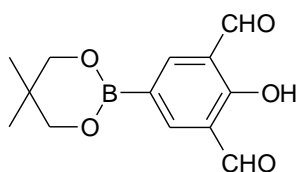
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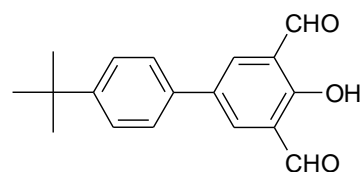
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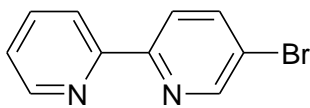
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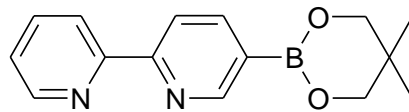
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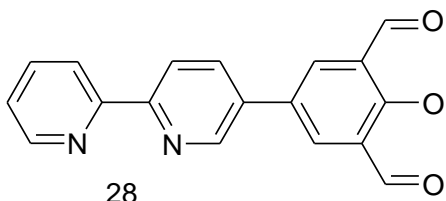
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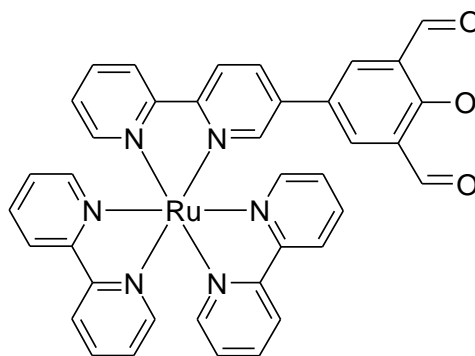
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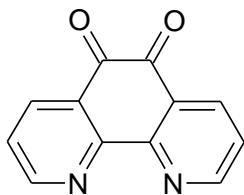
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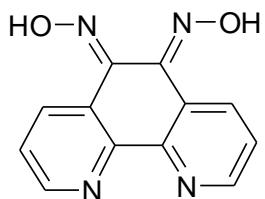
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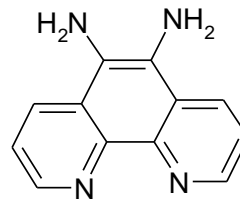
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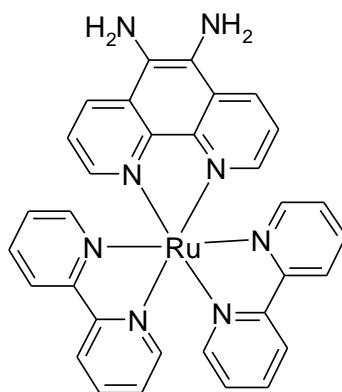
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31



32



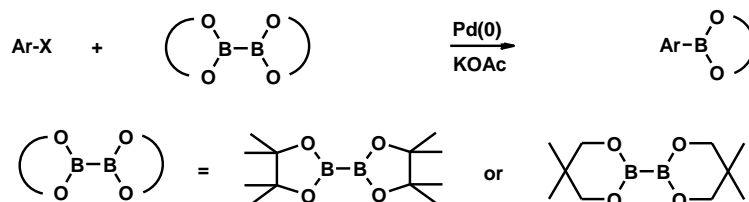
33

APPENDIX C:

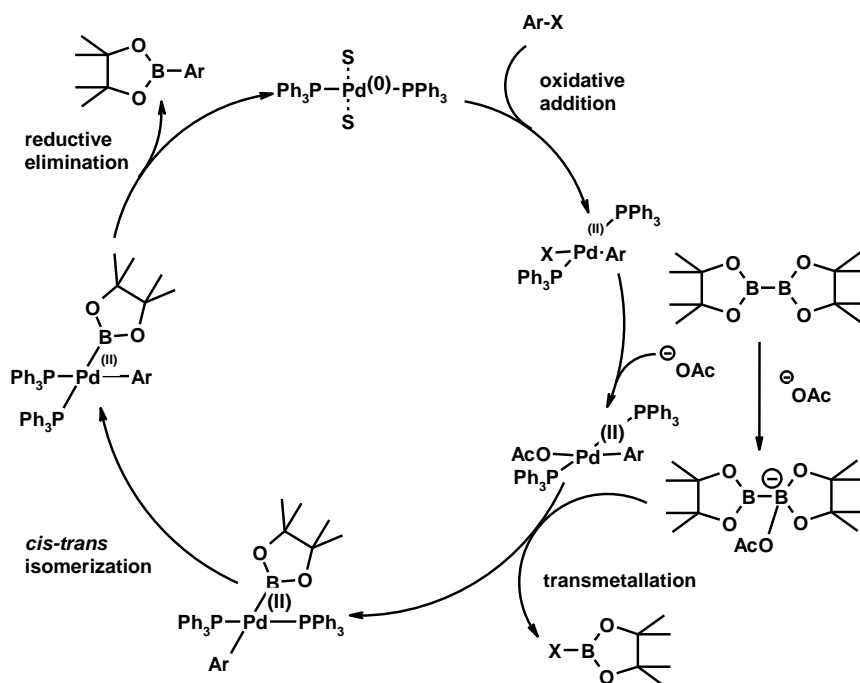
Mechanistic Schemes for Some Name Cross-Coupling Reactions

Miyaura Borylation

Overall Reaction:



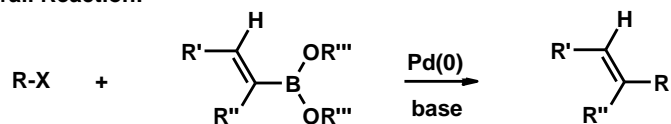
Proposed Mechanism:



Adapted from: Mundy, B.P.; Ellerd, M.G.; Favaloro, F.G., Jr. *Name Reactions and Reagents in Organic Syntheses*, Second Edition; John Wiley & Sons: Hoboken, NJ, 2005; pp 436,437.

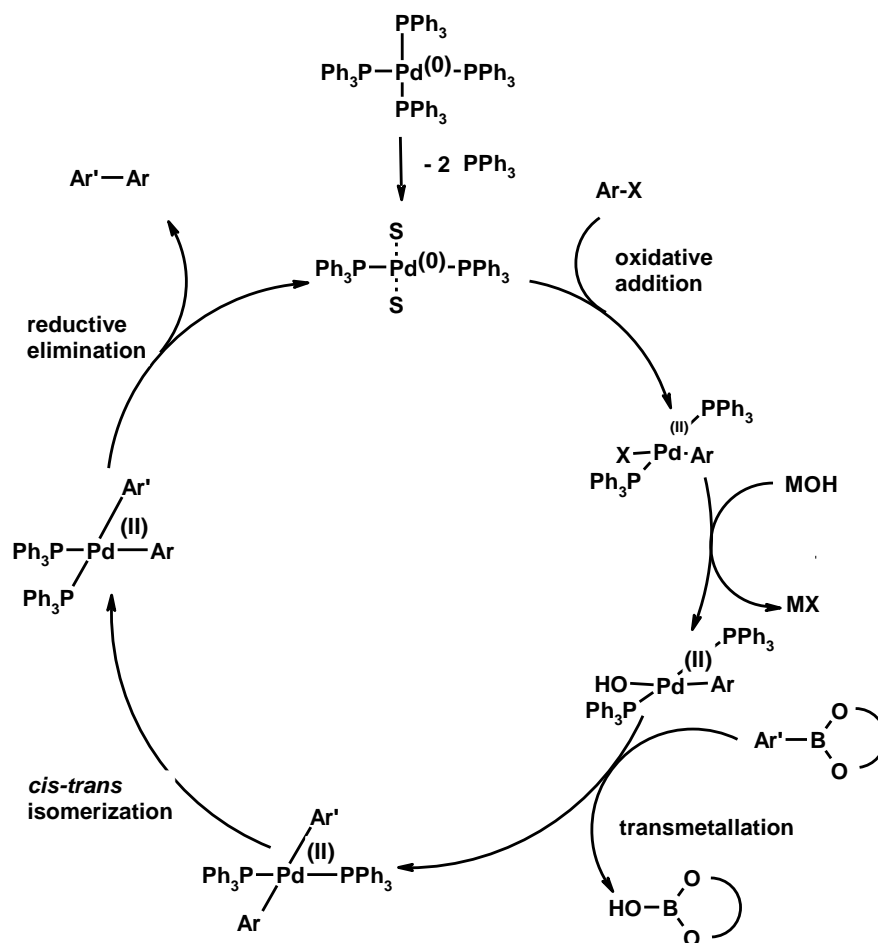
Suzuki Coupling (or Suzuki-Miyaura Coupling)

Overall Reaction:



Where X = I >> Br > OTf >> Cl

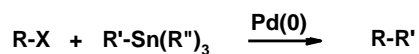
Proposed Mechanism:



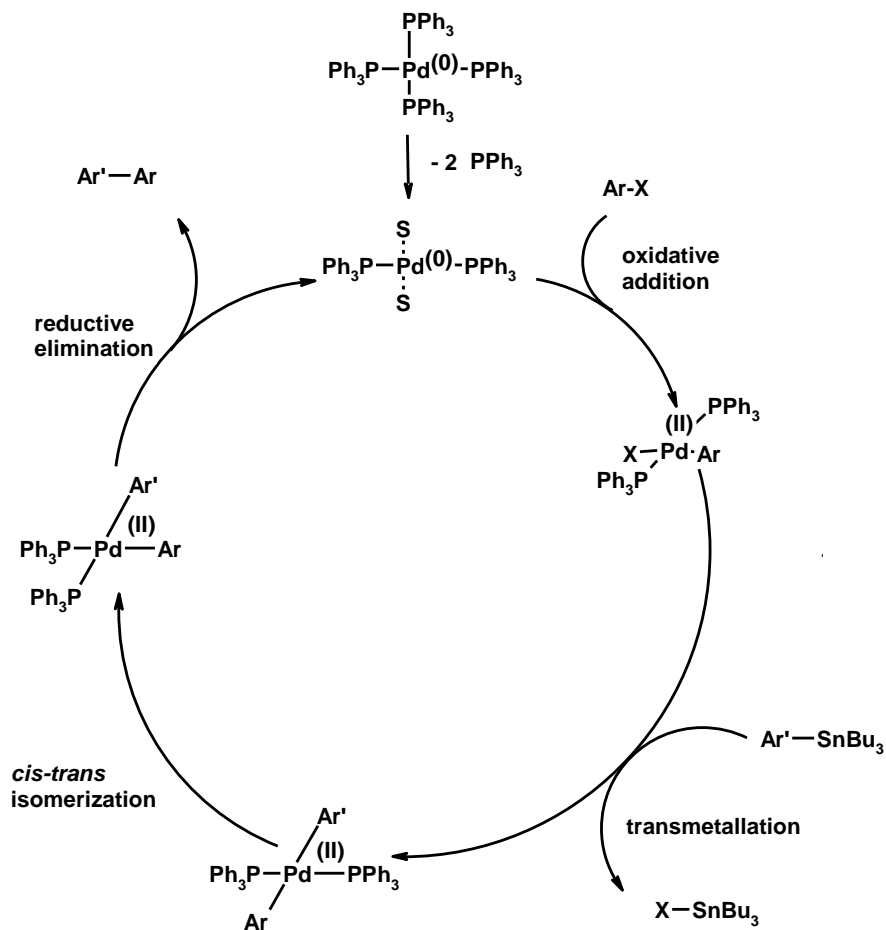
Adapted from: Mundy, B.P.; Eller, M.G.; Favaloro, F.G., Jr. *Name Reactions and Reagents in Organic Syntheses*, Second Edition; John Wiley & Sons: Hoboken, NJ, 2005; pp 636,637.

Stille Coupling

Overall Reaction:



Proposed Mechanism:



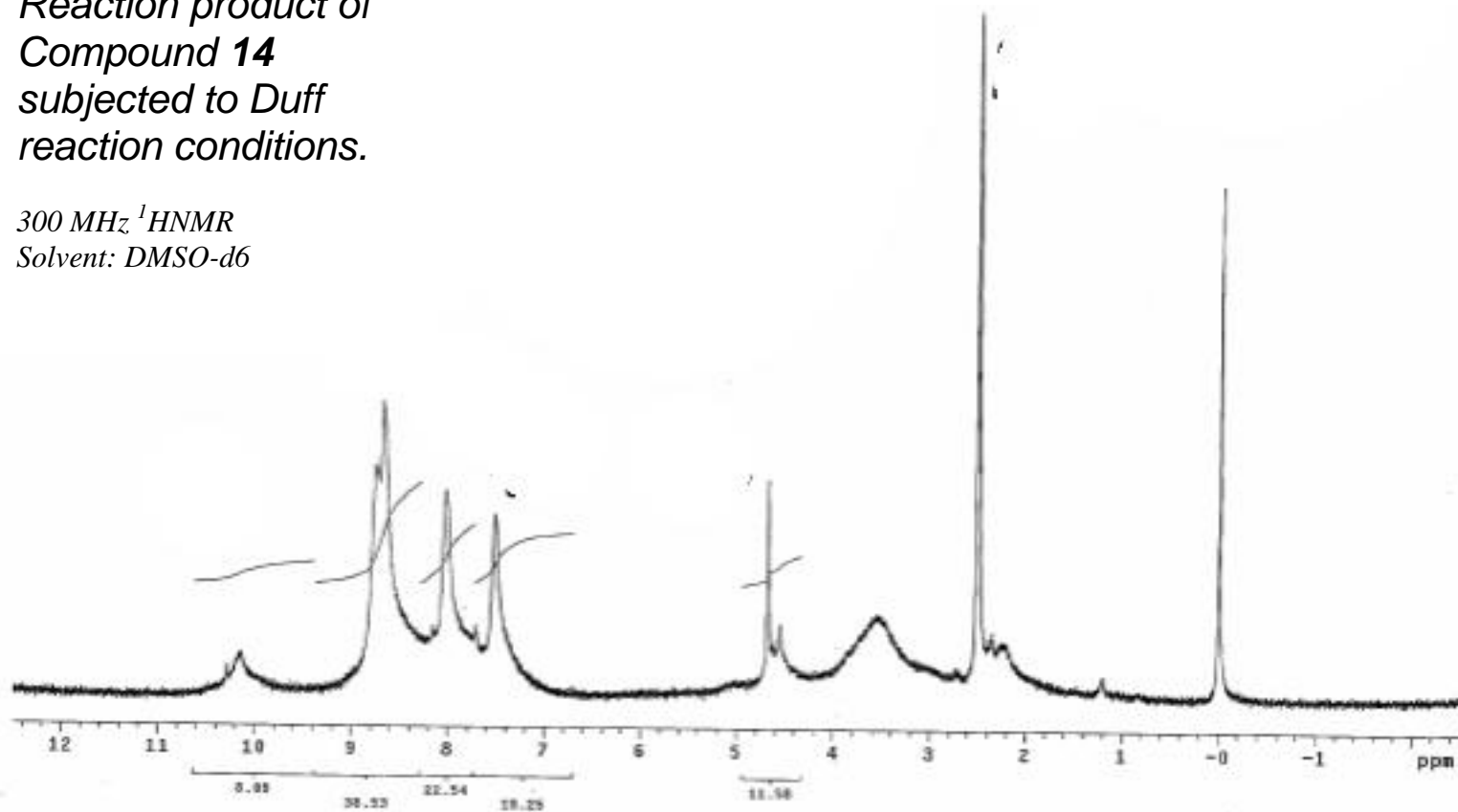
Adapted from: Mundy, B.P.; Ellerd, M.G.; Favaloro, F.G., Jr. *Name Reactions and Reagents in Organic Syntheses*, Second Edition; John Wiley & Sons: Hoboken, NJ, 2005; pp 620,621.

APPENDIX D:

Miscellaneous Analytical Data

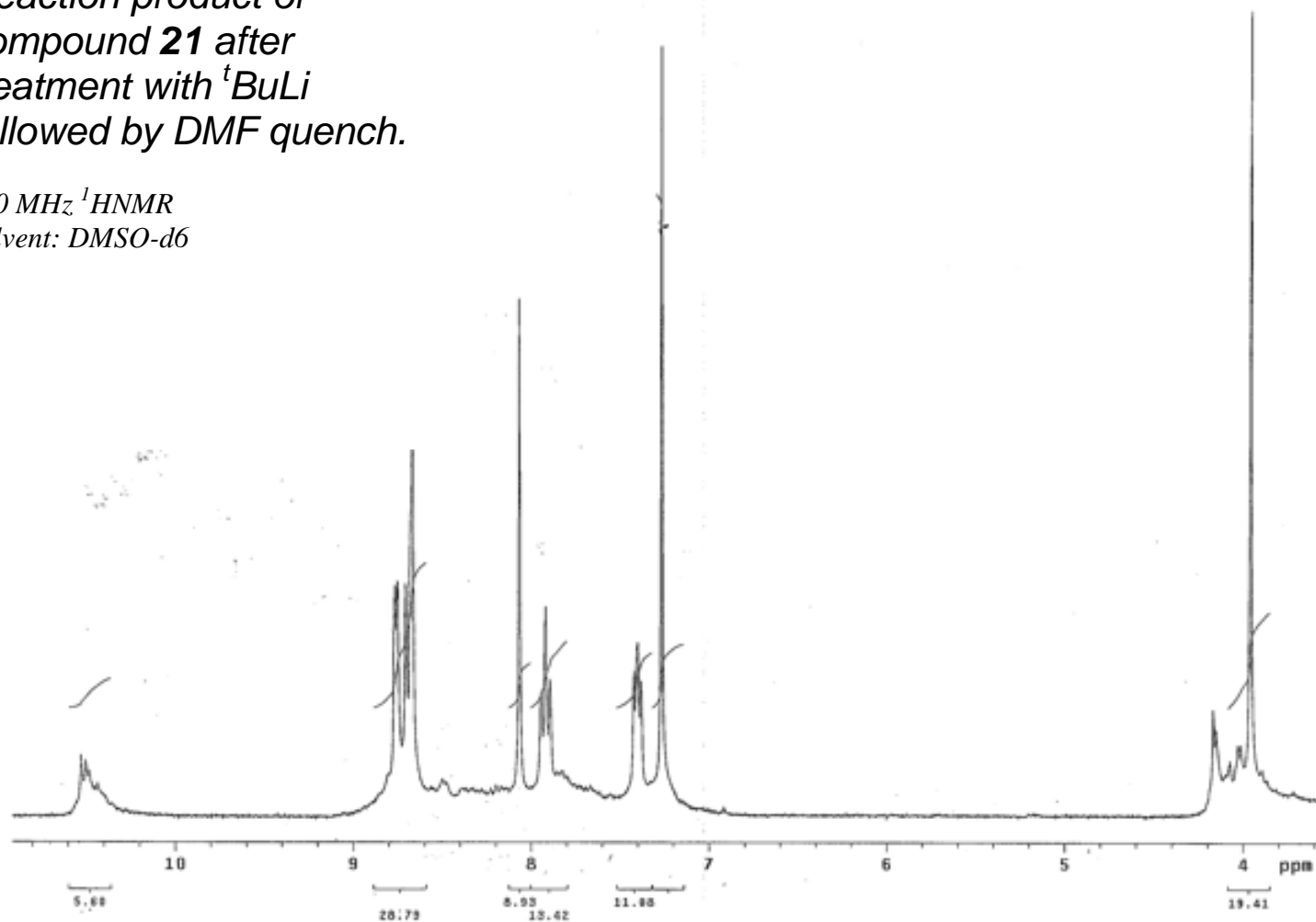
*Reaction product of
Compound **14**
subjected to Duff
reaction conditions.*

*300 MHz ^1H NMR
Solvent: DMSO- d_6*



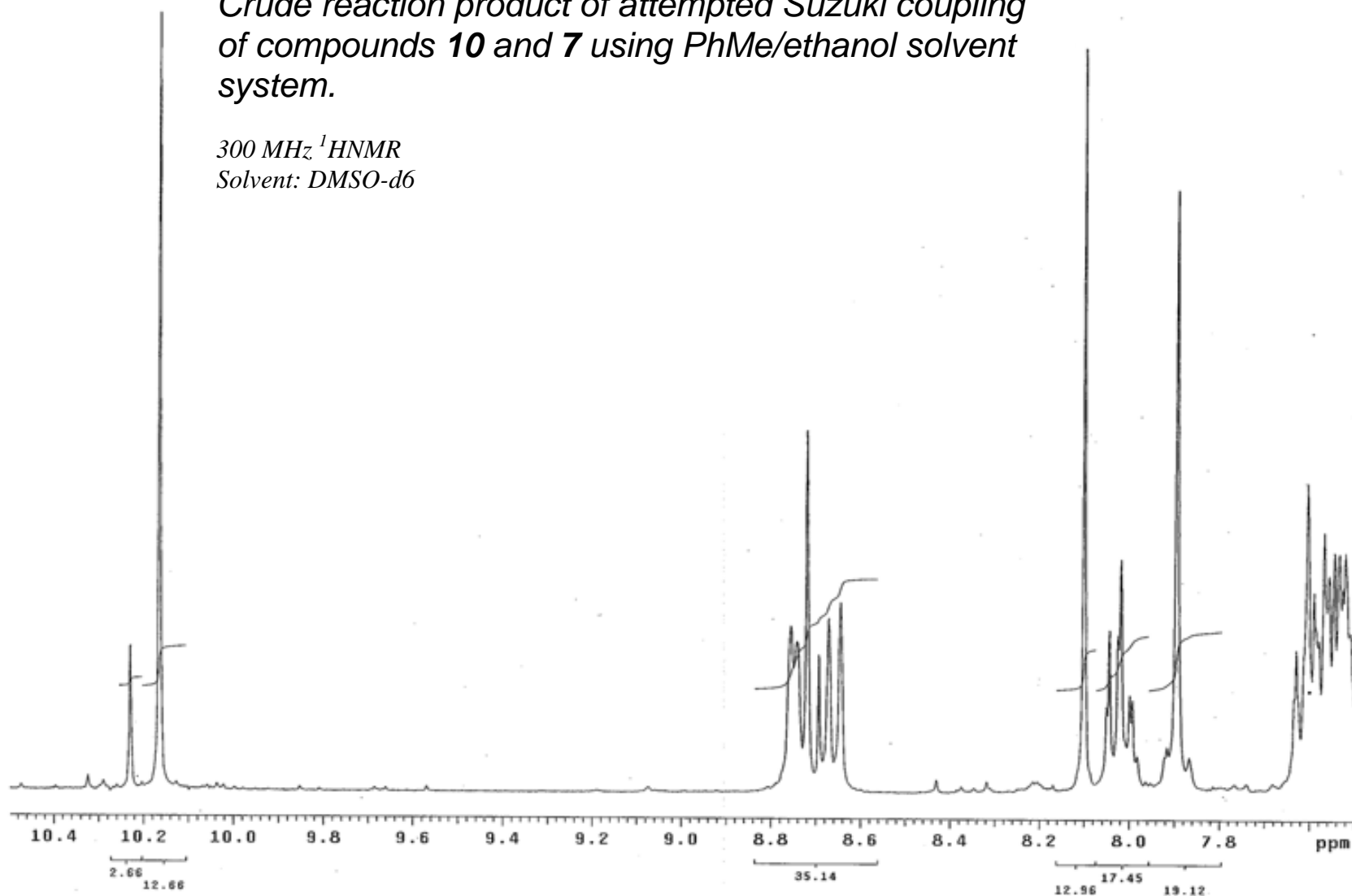
Reaction product of
compound **21** after
treatment with $t\text{BuLi}$
followed by DMF quench.

300 MHz $^1\text{H NMR}$
Solvent: DMSO- d_6



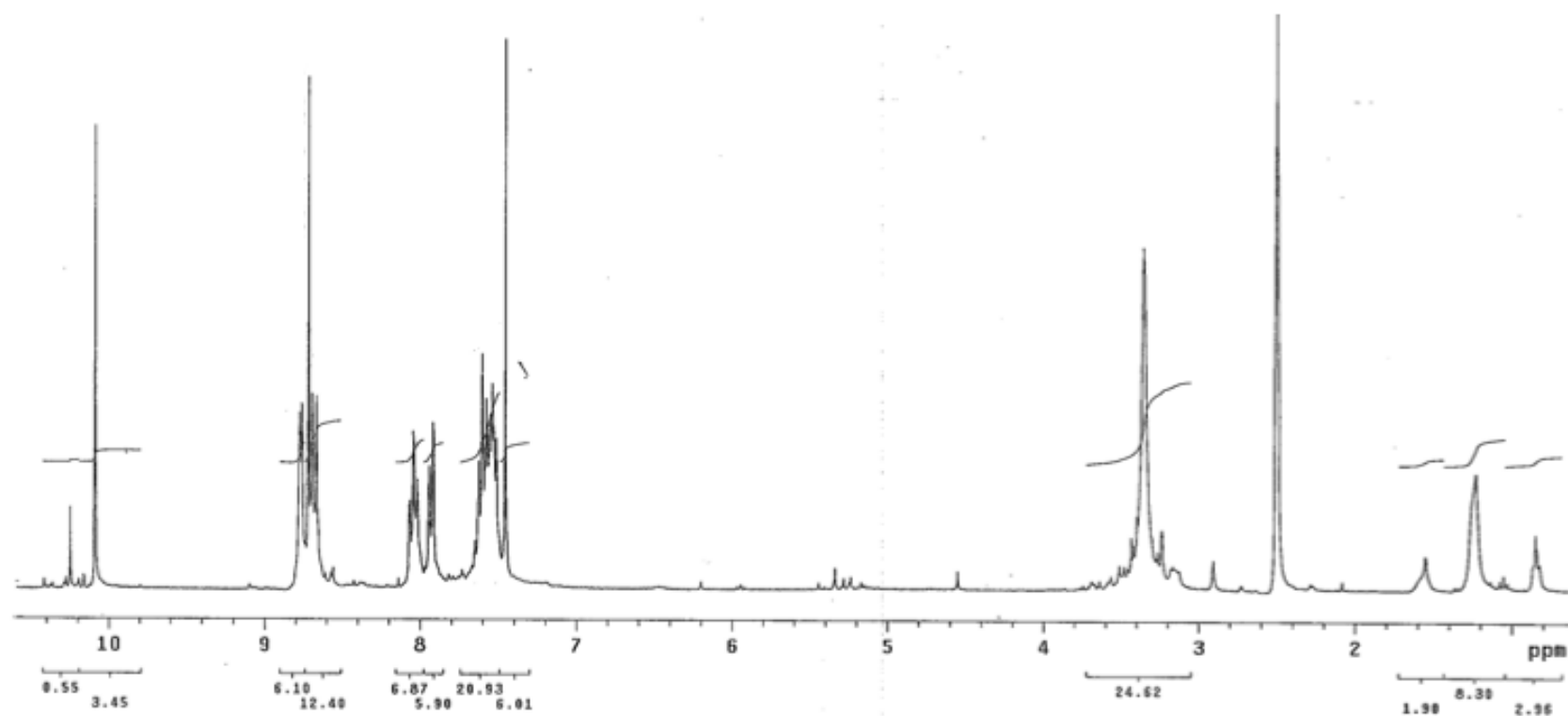
Crude reaction product of attempted Suzuki coupling
of compounds **10** and **7** using PhMe/ethanol solvent
system.

300 MHz ^1H NMR
Solvent: DMSO- d_6



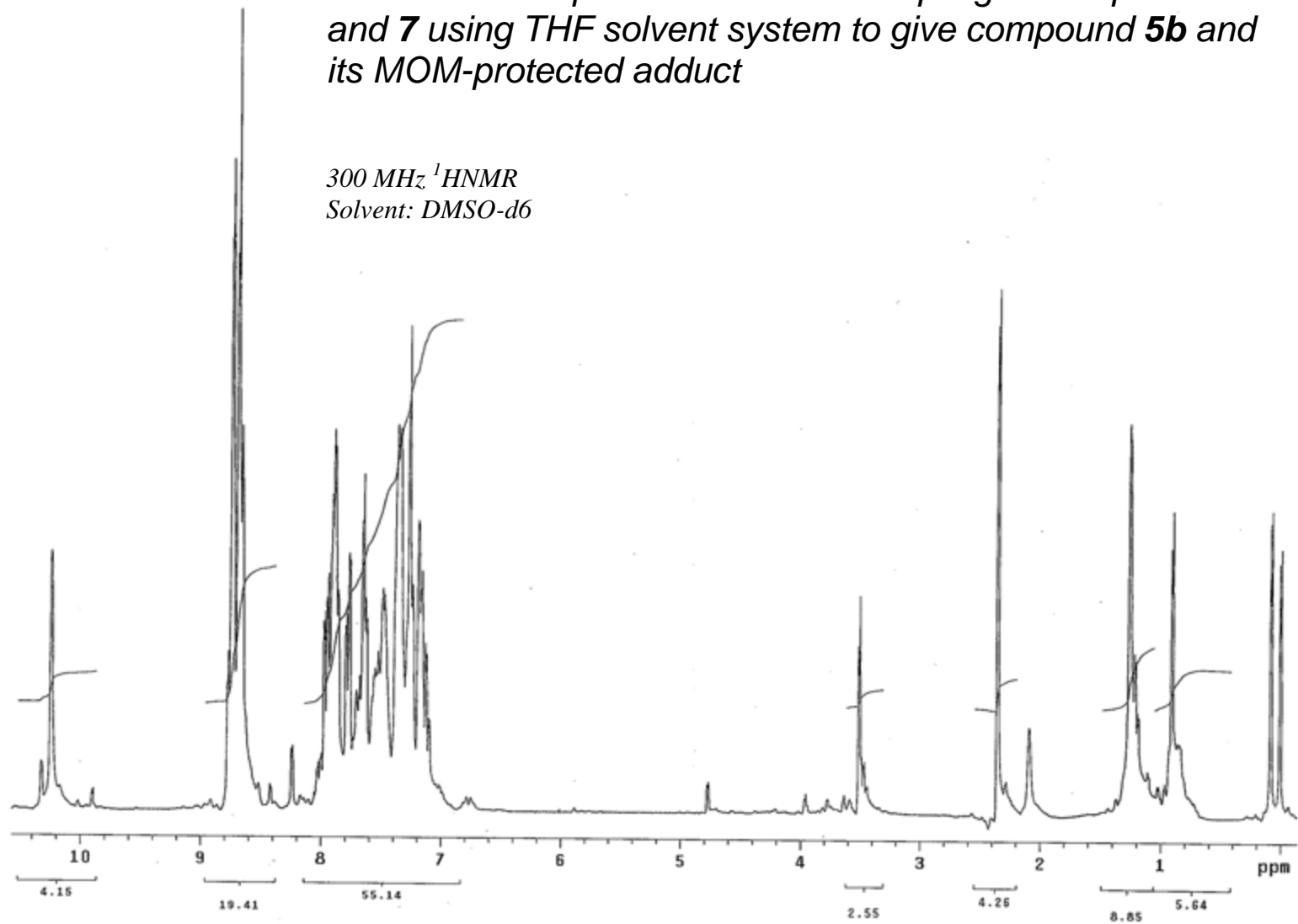
Crude reaction product of attempted Suzuki coupling of compounds **11** and **7** using PhMe/ethanol solvent system.

300 MHz ^1H NMR
Solvent: DMSO- d_6

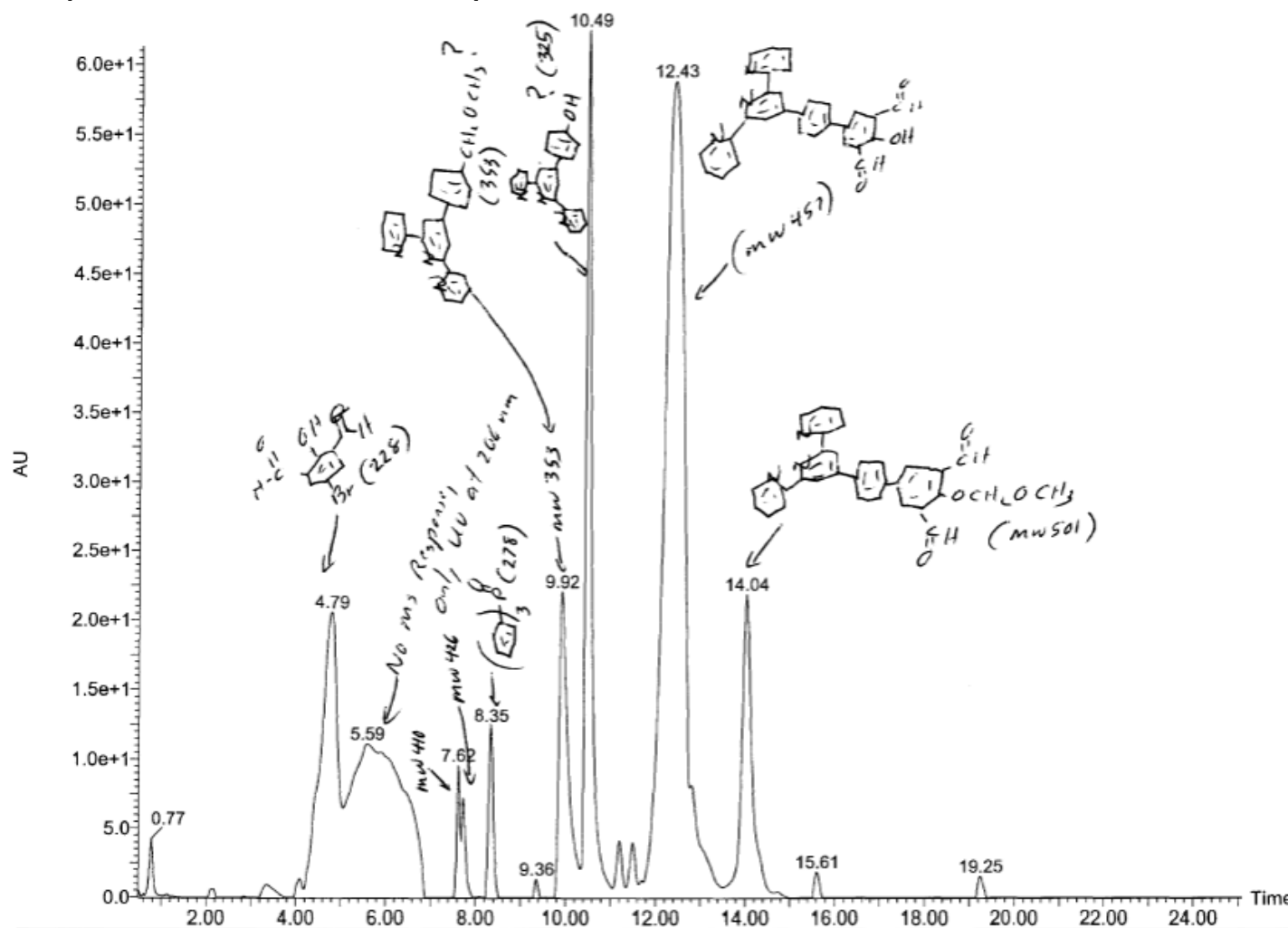


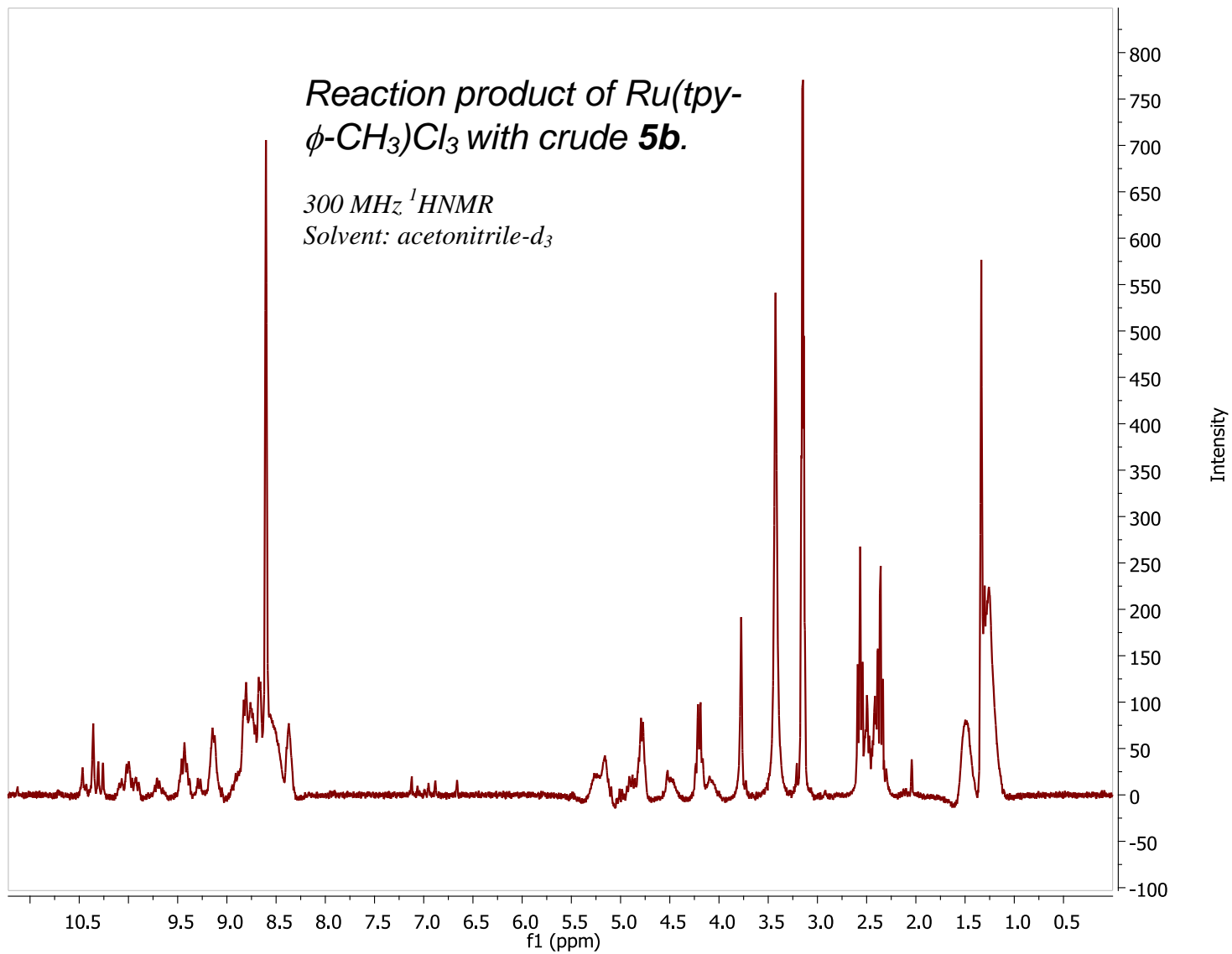
*Crude reaction product of Suzuki coupling of compounds **11** and **7** using THF solvent system to give compound **5b** and its MOM-protected adduct*

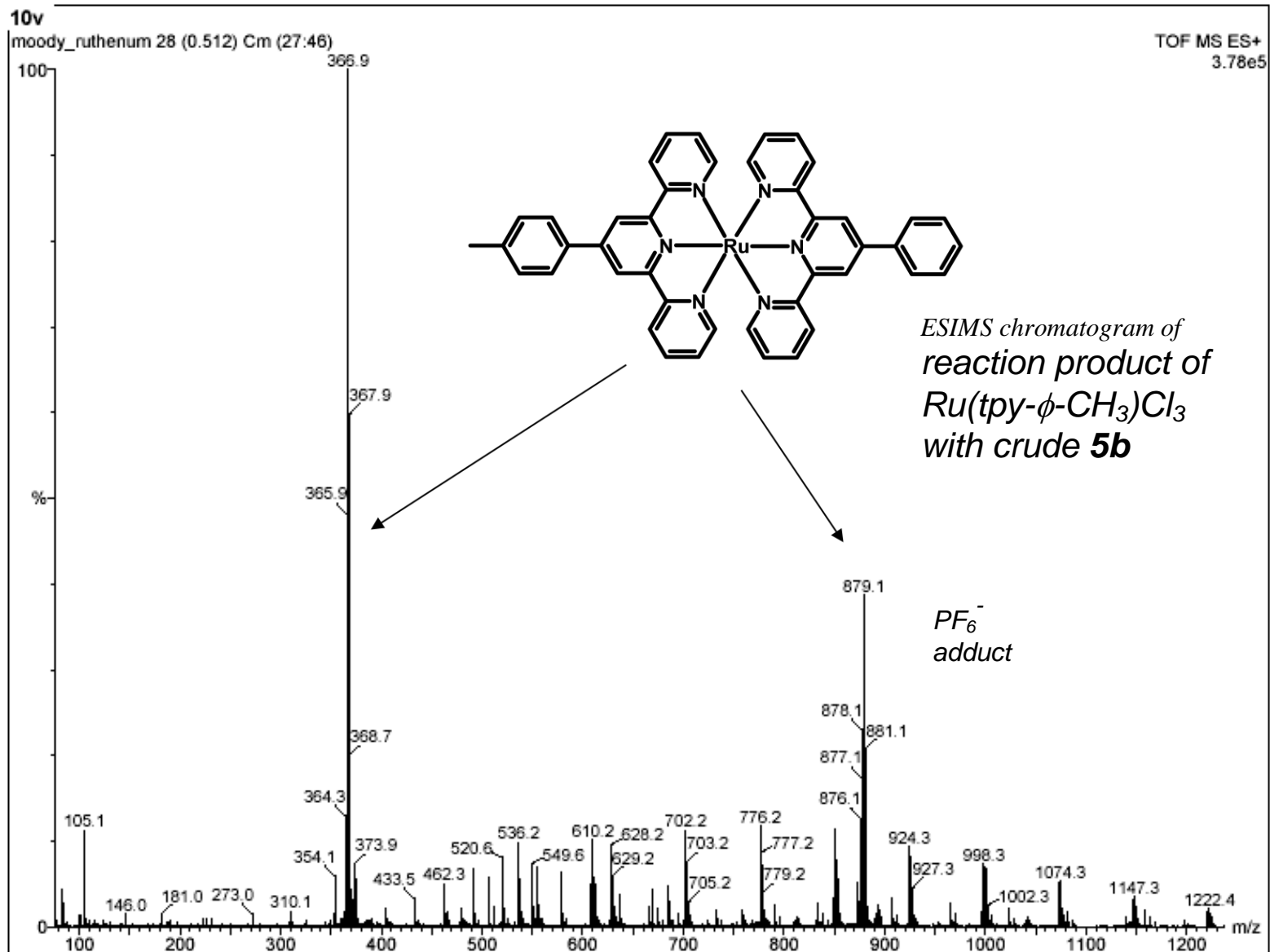
*300 MHz ^1H NMR
Solvent: DMSO- d_6*



Uv-vis chromatograms from electrospray LC-MS showing
 Crude reaction product of Suzuki coupling of compounds **11** and **7** to give
 compound **5b** and its MOM-protected adduct







VITA

L. SHANE MOODY

- Personal Data: Date of Birth: September 25, 1958
 Place of Birth: Elizabethton, Tennessee
 Marital Status: Married
- Education: Public Schools, Elizabethton City and Johnson County,
 Tennessee
 B.S. Chemistry (ACS Certification), East Tennessee State
 University, Johnson City, Tennessee 1993
 M.S. Chemistry, East Tennessee State University, Johnson
 City, Tennessee 2008
- Professional Experience: Sign Artist/Manufacturer, Cookeville, Tennessee; Ames,
 Iowa; Elizabethton, Tennessee; 1977-1992
 Researcher, Polymers Technology, Eastman Chemical
 Company, Kingsport, Tennessee, 1992-present
- Issued US Patents: Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G.
 G.; Ponasik, J. A., Jr.; Smith, T. W.; Pearson, J. C.;
 Barrett, A. G. M. *Catalysts containing N-pyrrolyl*
 substituted nitrogen donors. US 7,3419,084 January
 15, 2008
 Mackenzie, P. B.; Moody, L. S.; Ponasik, J. A.; Farthing, A.
 K. *Productivity catalysts and microstructure control.*
 US 7,056,996 June 6, 2006
 Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G.
 G.; Ponasik, J. A., Jr.; Smith, T. W.; Pearson, J. C.;
 Barrett, A. G. M. *Catalysts containing per-ortho aryl*

- substituted aryl or heteroaryl substituted nitrogen donors.* US 6,946,532 September 20, 2005
- Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A., Jr.; Smith, T. W.; Pearson, J. C.; Barrett, A. G. M. *Catalysts containing per-ortho aryl substituted aryl or heteroaryl substituted nitrogen donors.* US 6,844,446 January 18, 2005
- Ponasik, J.A.,Jr.; McDevitt, J. P.; Killian; C. M.; Mackenzie; P.B.; Moody, L.S. *Catalyst compositions for the polymerization of olefins.* US 6,844,404 January 18, 2005
- Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A., Jr.; Smith, T. W.; Pearson, J. C.; Barrett, A. G. M. *Catalysts containing N-pyrrolyl substituted nitrogen donors.* US 6,825,356 November 30, 2004
- Mackenzie; P.B.; Moody, L.S.; Killian, C.M.; Lavoie; G.G. *Supported group 8-10 transition metal olefin polymerization catalysts.* US 6,822,062 November 23, 2004
- Ponasik, J. A., Jr.; Moody, L.S.; Mackenzie; P.B. *Process for the preparation of ligands for olefin polymerization catalysts.* US 6,706,891 March 16, 2004
- Mackenzie; P.B.; Moody, L.S.; Killian, C.M.; Lavoie; G.G. *Supported group 8-10 transition metal olefin polymerization catalysts.* US 6,660,677 December 9, 2003
- Mackenzie; P.B.; Killian, C.M.; Moody, L.S.; McDevitt, J. P. *Group 8-10 transition metal olefin polymerization catalysts.* US 6,656,869 December 2, 2003
- Killian, C.M.; Mackenzie; P.B.; Lavoie; G.G.; Ponasik, J. A.,

Jr.; Moody, L.S. *Mixed olefin polymerization catalysts, processes employing such catalysts, and polymers obtained therefrom.* US 6,620,896
September 16, 2003

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