

Toward Liquid Crystalline Supramolecular Squares based on Platinum(II) Diimine Complexes

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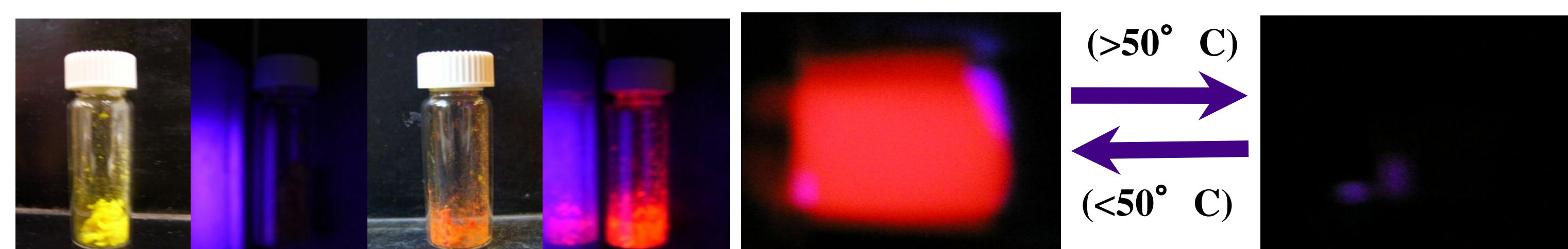
Abstract

Bipyridine complexes of platinum (II) complexes have long been recognized to possess a host of interesting, and potentially useful, structural, optical and electronic properties. By elaborating the structure of the bipyridine moiety of [bpyPt(II)Cl₂] with a pair of β -branched Guerbet ester fragments, liquid-crystalline derivatives of this unique chromophore have been prepared. In several cases, the liquid-crystalline behavior was observed to persist well below room temperature. Efforts to utilize acetylide linkages to couple either multiple liquid-crystalline bipyridine platinum fragments or a mixture of these bipyridine fragments and alkylated carbazole moieties are currently underway. As part of these efforts, the synthesis and reactivity of model ethynylaryl "corner" complexes will be presented. The optical and electronic behavior of this new series of materials, as well as progress toward the creation of the targeted liquid crystalline supramolecular squares based on diethynylaryl linkers, will be presented.

Introduction / Goals

Bipyridine platinum(II) complexes with a the general formula bpyPtX₂ are known to possess a variety of interesting physical properties. These properties depend strongly on both molecular structural features (e.g. the identity of X or groups attached to the bpy moiety) and the supramolecular aggregation of the complexes.

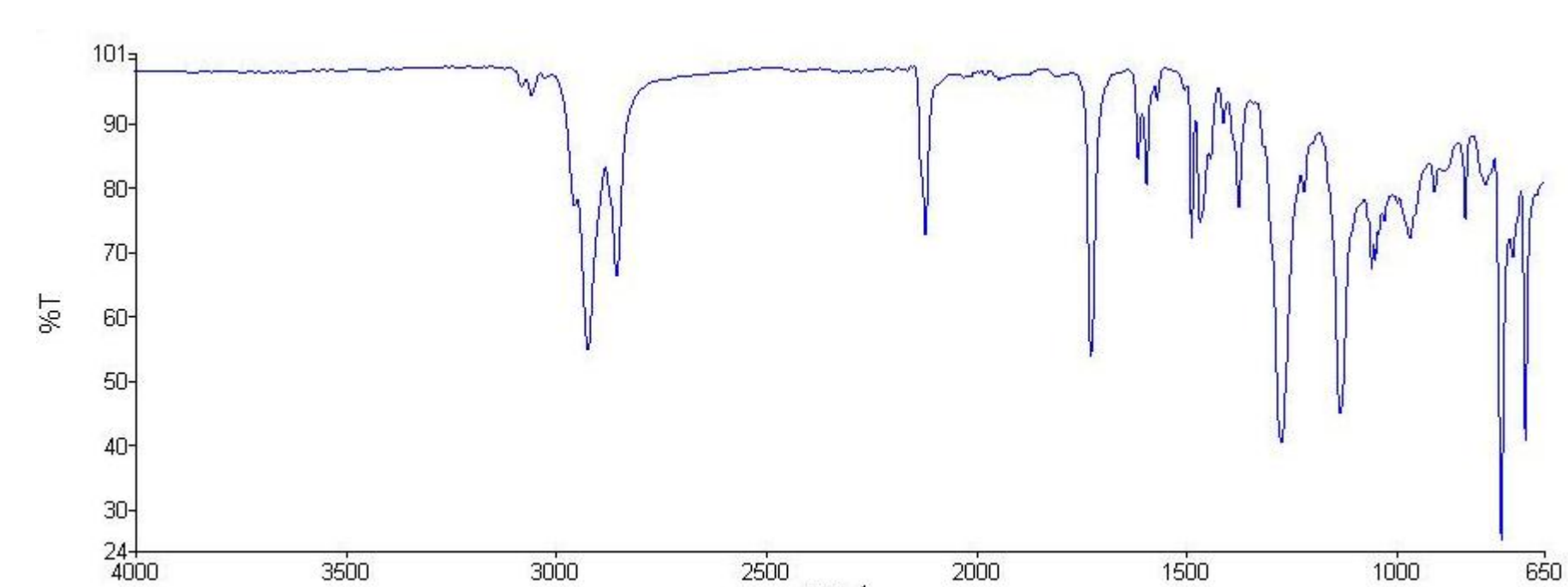
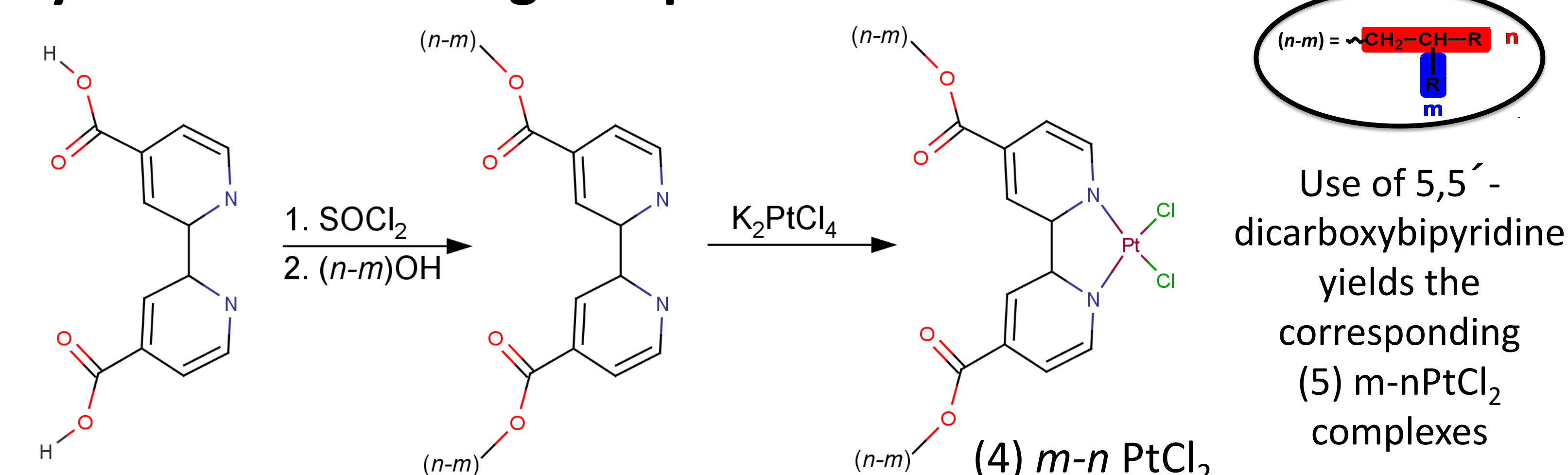
We have successfully synthesized a series of liquid-crystalline derivatives of bpyPtCl₂ by coupling a pair of β -branched Guerbet alcohol fragments to the bipyridine unit. These materials display interesting phase-dependent optical properties.



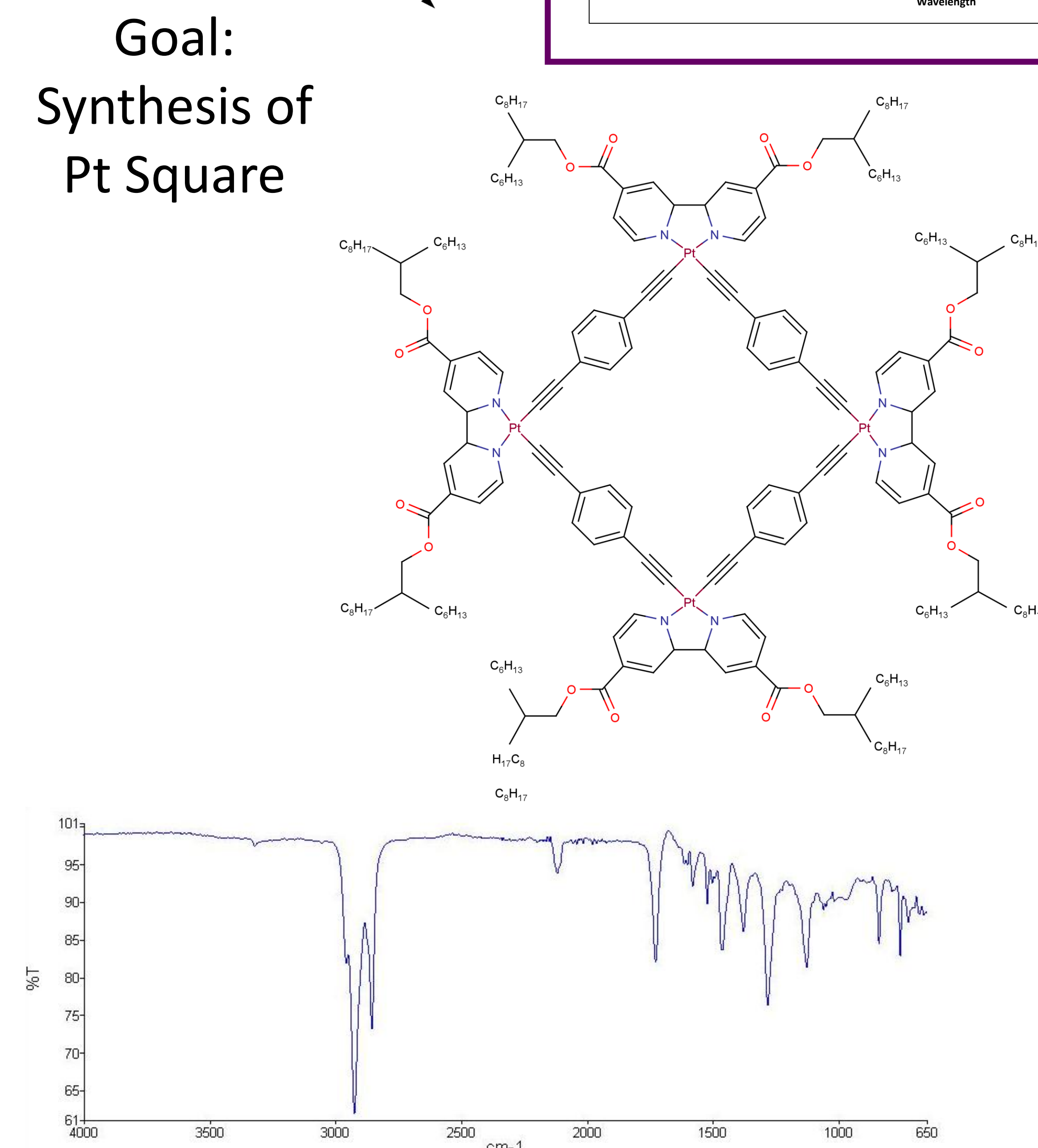
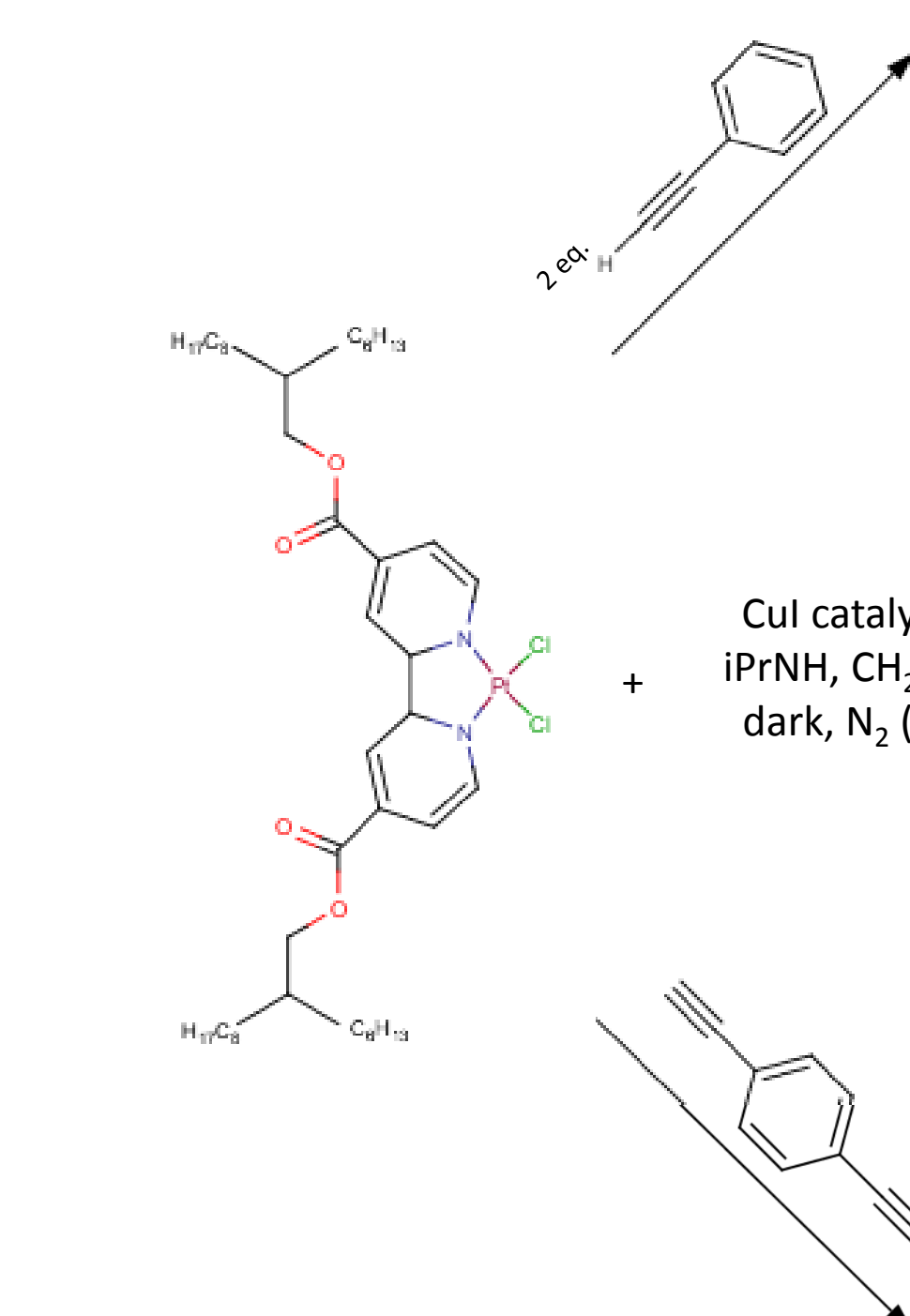
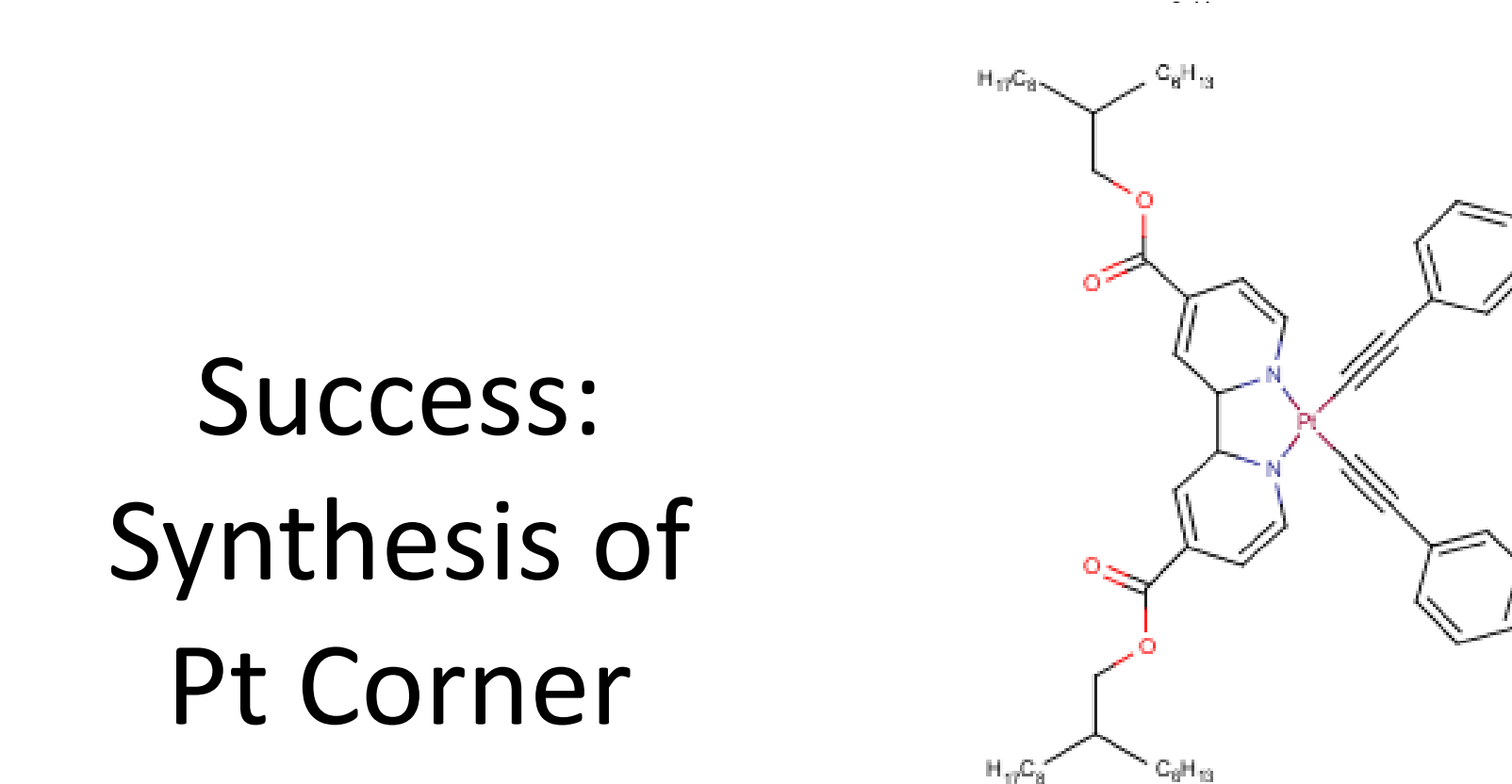
(4)6-2PtCl₂ exists in two polymorphic forms--yellow, non-luminescent and orange, luminescent. These two forms can be accessed either from solution or via a solid-state phase transition. (4)10-6PtCl₂, which was used in this study, undergoes a similar change from a luminescent to a nonluminescent liquid crystalline phase.

Since platinum(II) acetylide complexes show a host of potentially useful properties, such as electroluminescence for use in devices such as OLEDs, we sought to create a new class of model acetylide compounds and use the knowledge gained in these studies to construct two novel classes of supramolecular squares, which should possess unique and interesting physical properties.

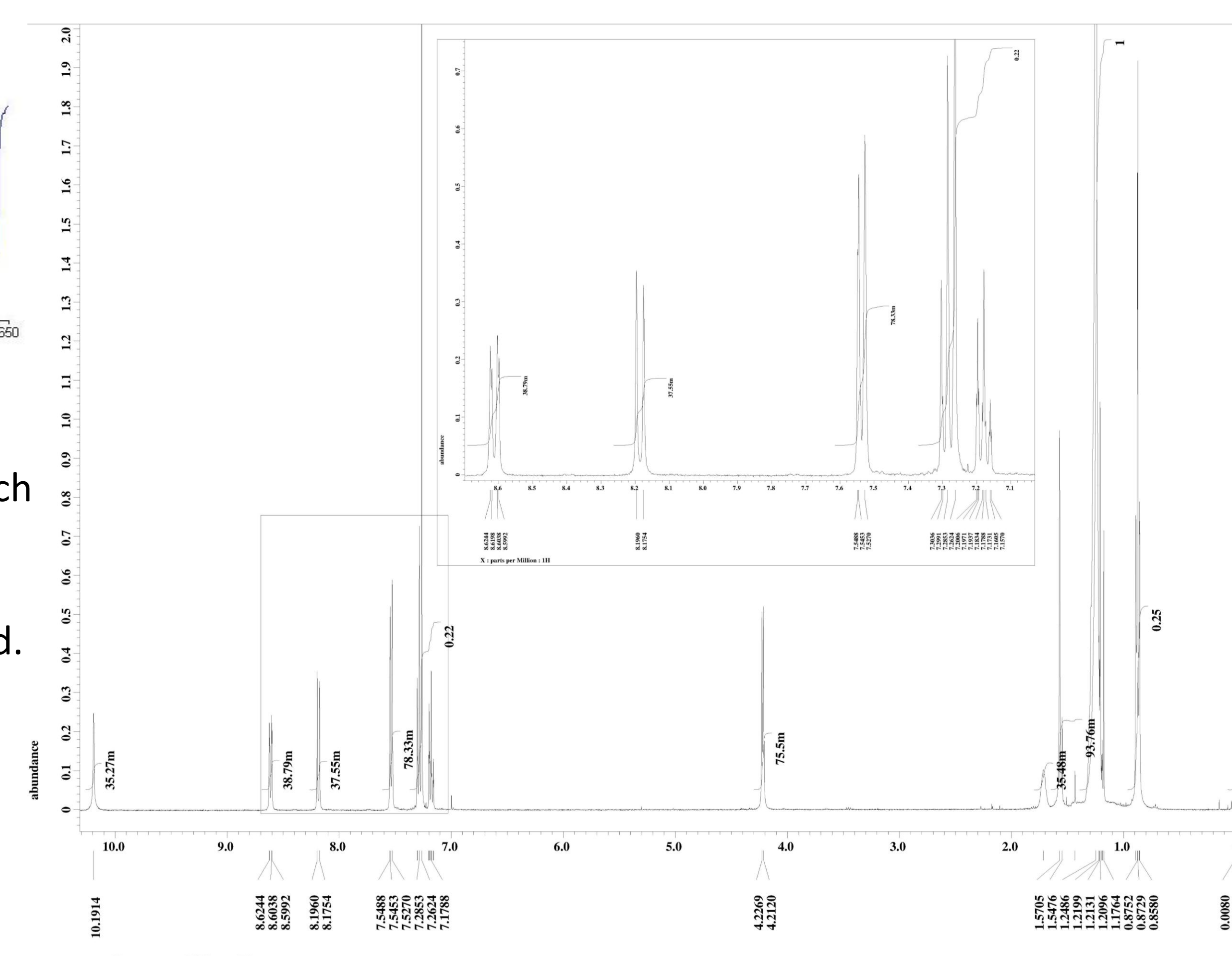
Synthesis of starting complexes



The infrared spectra of the di(phenyl acetylide)₂ platinum (II) corner shows the acetylide C≡C stretch at 2118 cm⁻¹ and the aromatic stretch at 3050 cm⁻¹. The C-H stretch seen in the Pt square IR spectra is absent because the acetylide is double substituted.

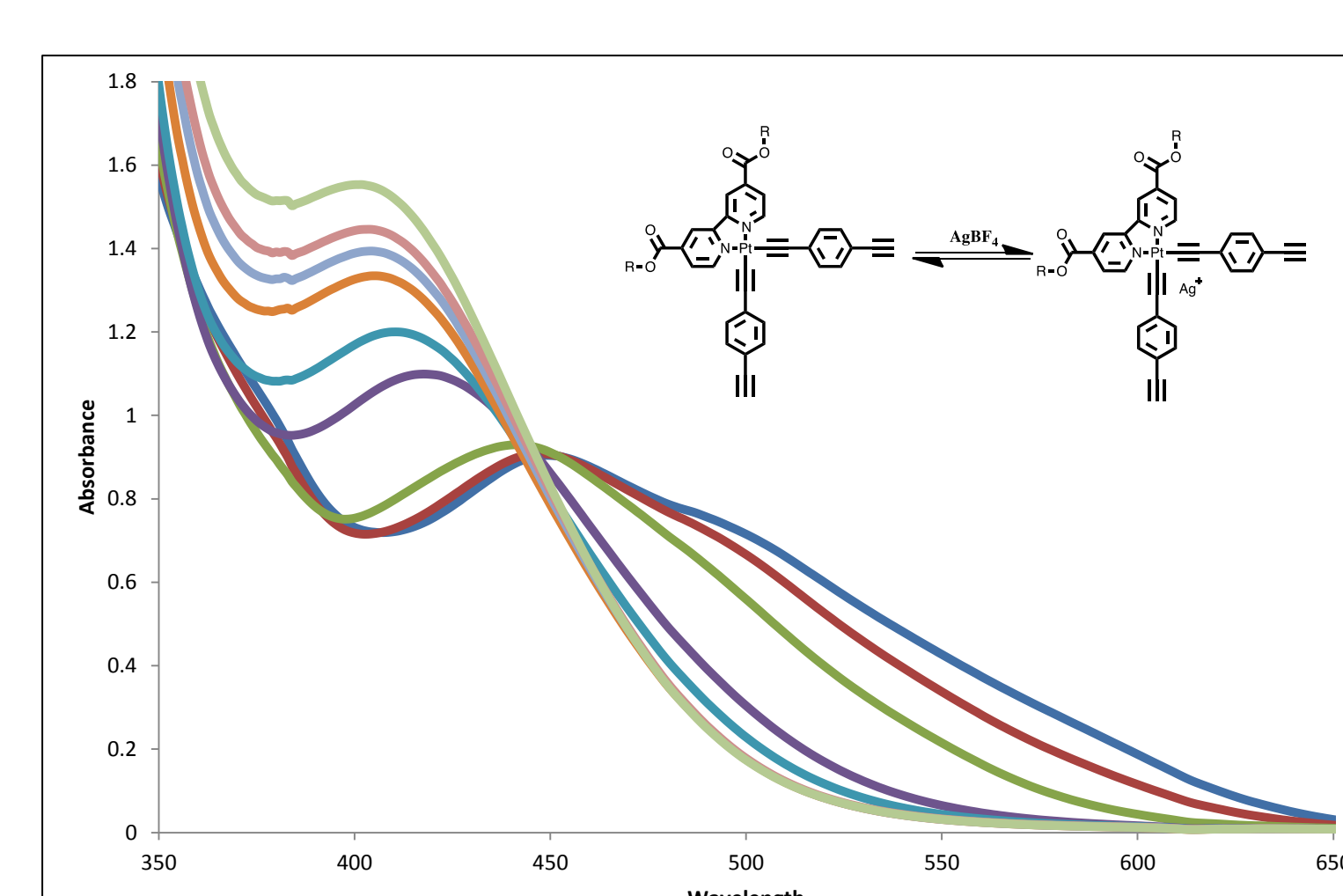


The infrared spectra of of the Pt square shows the acetylenic stretches at 3318 and 2116 cm⁻¹.

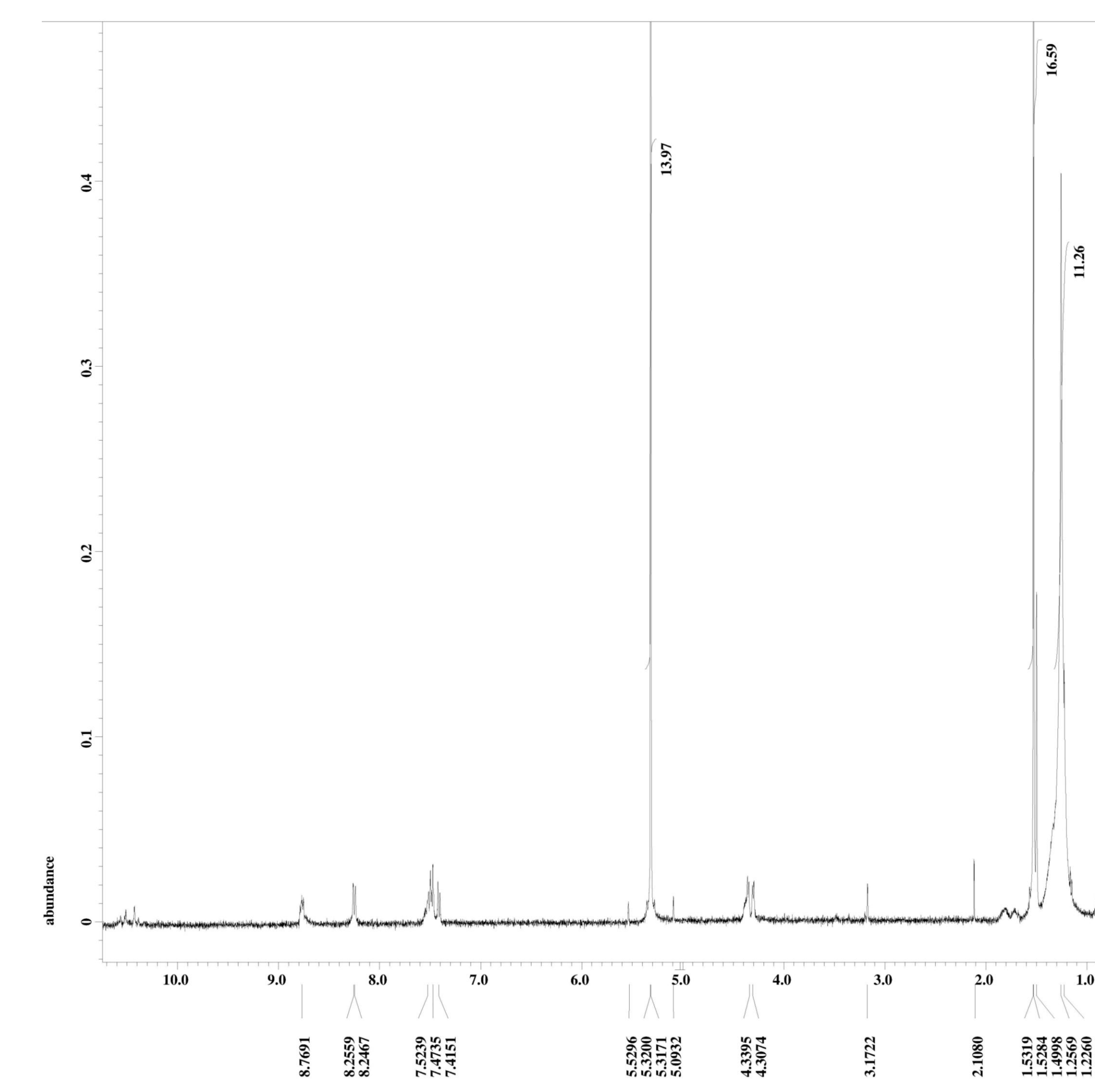
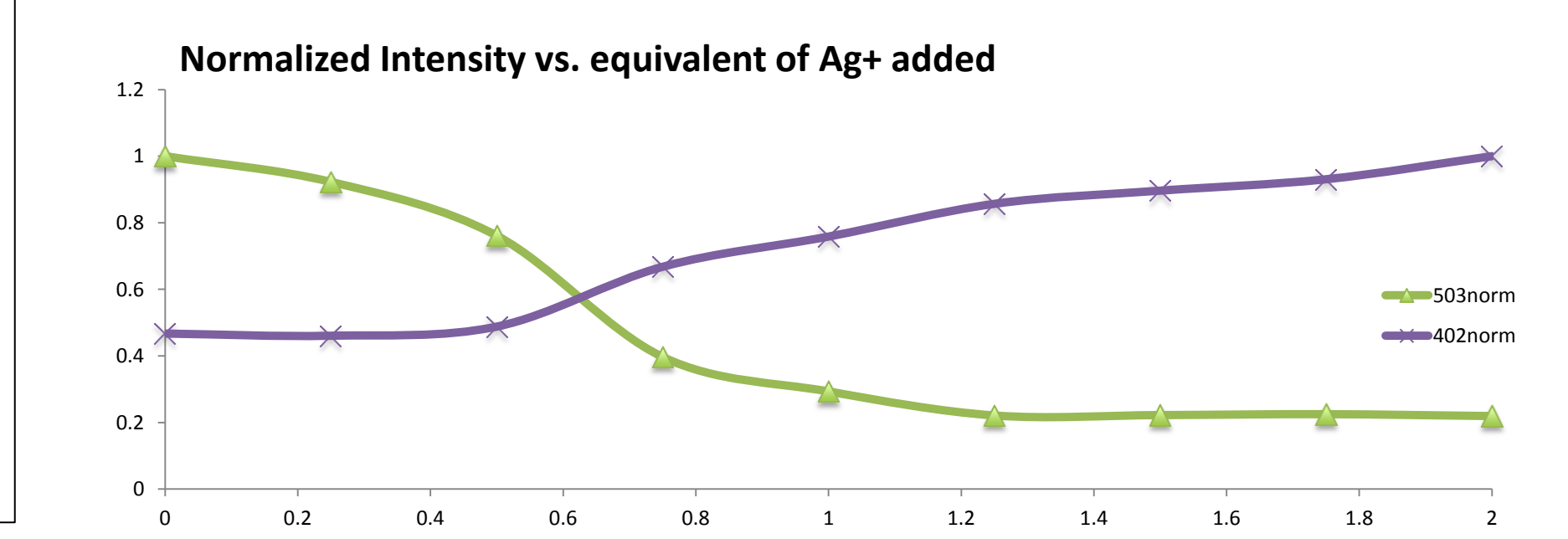


¹H NMR of the di(phenyl acetylide)₂ platinum (II) corner obtained at 400 MHz in CDCl₃ shows the expected number of signals in the aromatic region.

Titration of Platinum 1,4-diethynylbenzene Corner With AgBF₄

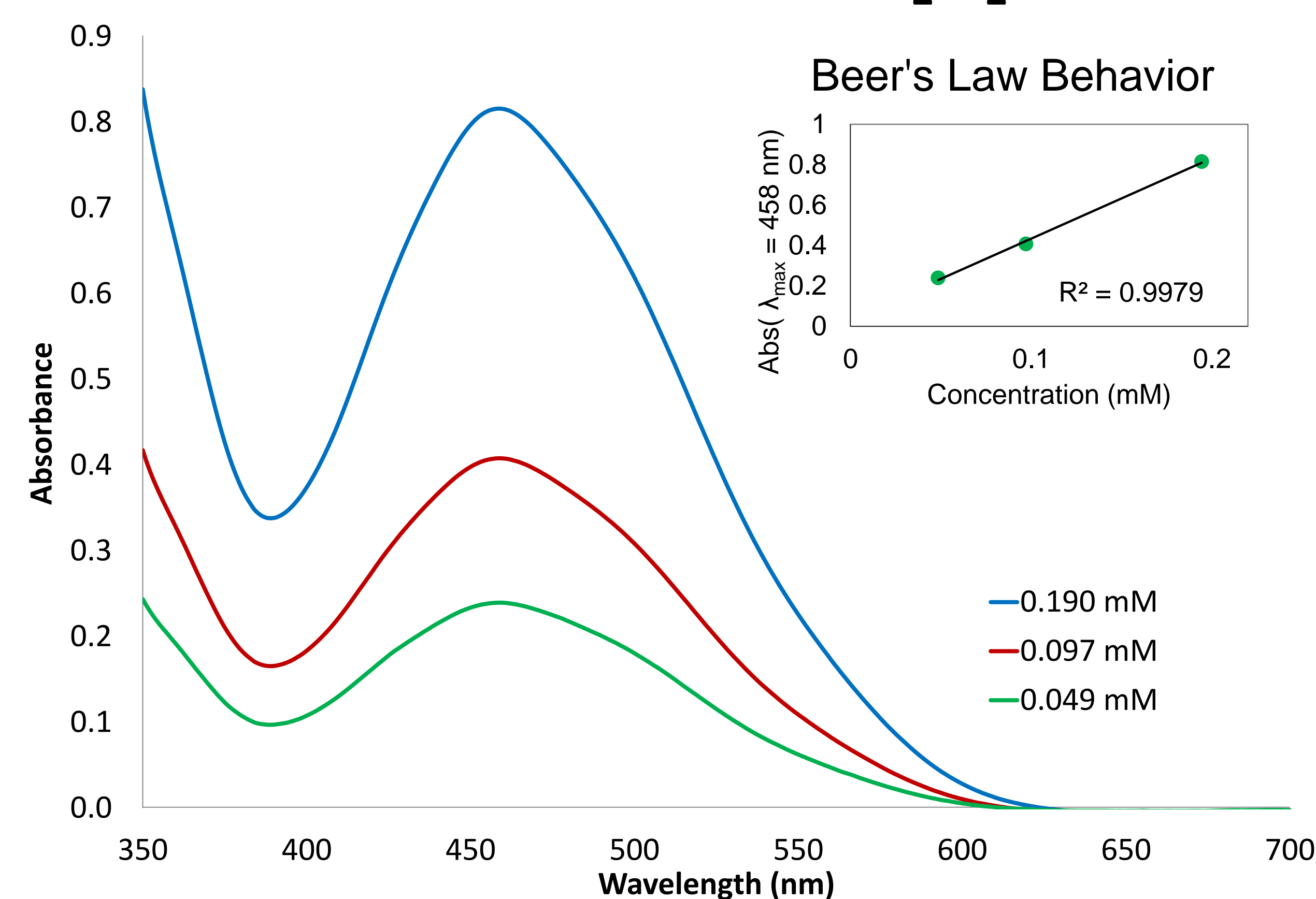


A Titration of the corner piece with a solution of AgBF₄ yielded the UV-Vis spectra to the left with an isosbestic point at about 455 nm. This indicates an equilibrium between two species.



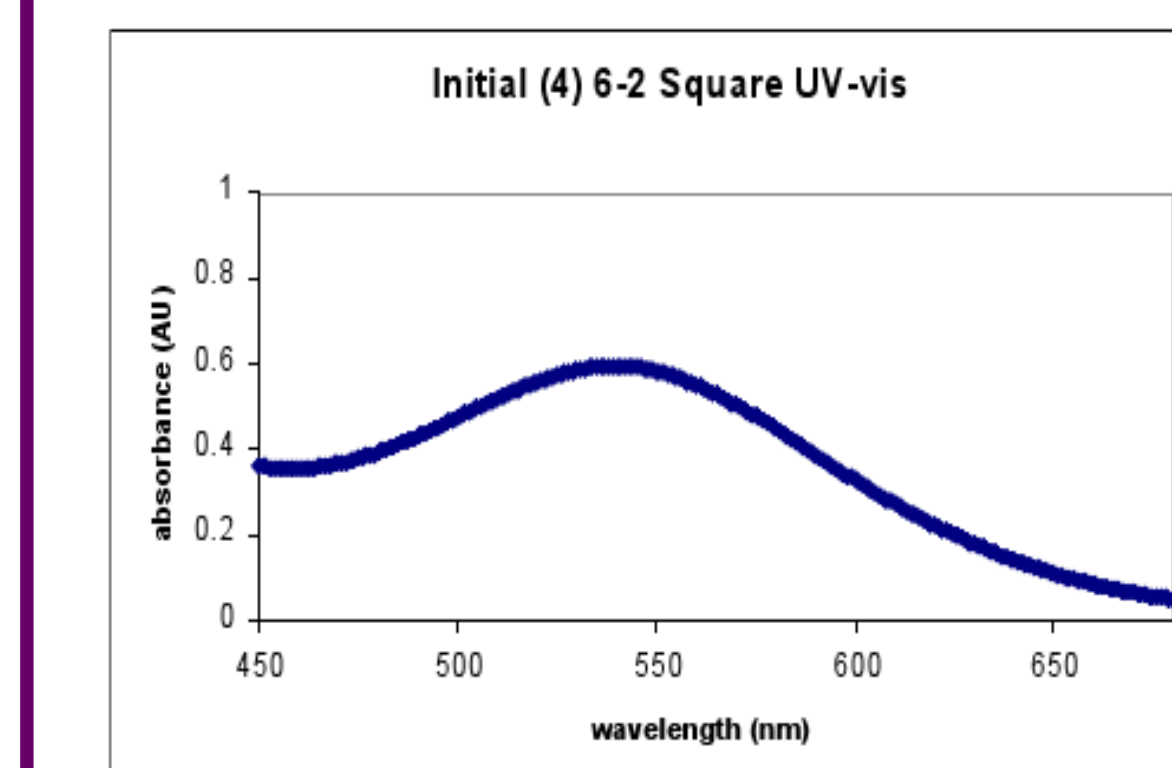
¹H NMR of the diethynylbenzene platinum (II) square obtained at 400 MHz in CD₂Cl₂.

UV-Vis Data for Pt Corner in CH₂Cl₂

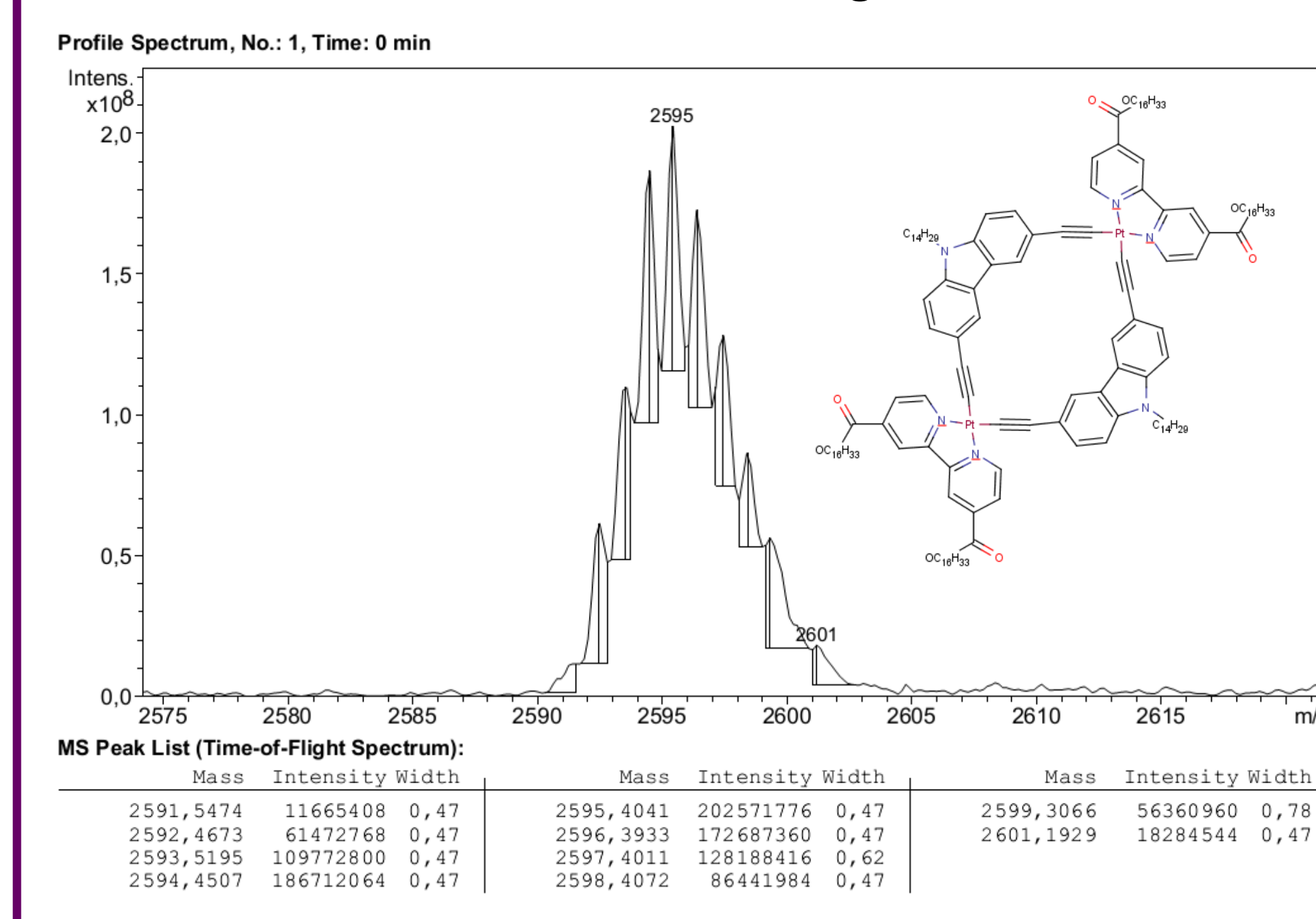


The Beer's Law behavior of the Pt(II) phenyl acetylide corners indicate the lack of supramolecular aggregation.

Mass Spectrum of Mixed Carbazole-Platinum Squares



The product of this reaction is deeply purple in color (λ_{max} = 640 nm). The NMR spectrum shows the expected number of signals in the aromatic region.



Future Work

- Purify and characterize the products of the Pt square reaction
- Characterize square and corner materials by mass spectrometry
- Characterize the phase behavior of square and corner complexes

Pt corner and square synthesis adapted from Lu, W.; *et al. Chem. Eur. J.* **2003**, *9*, 6155-6166.