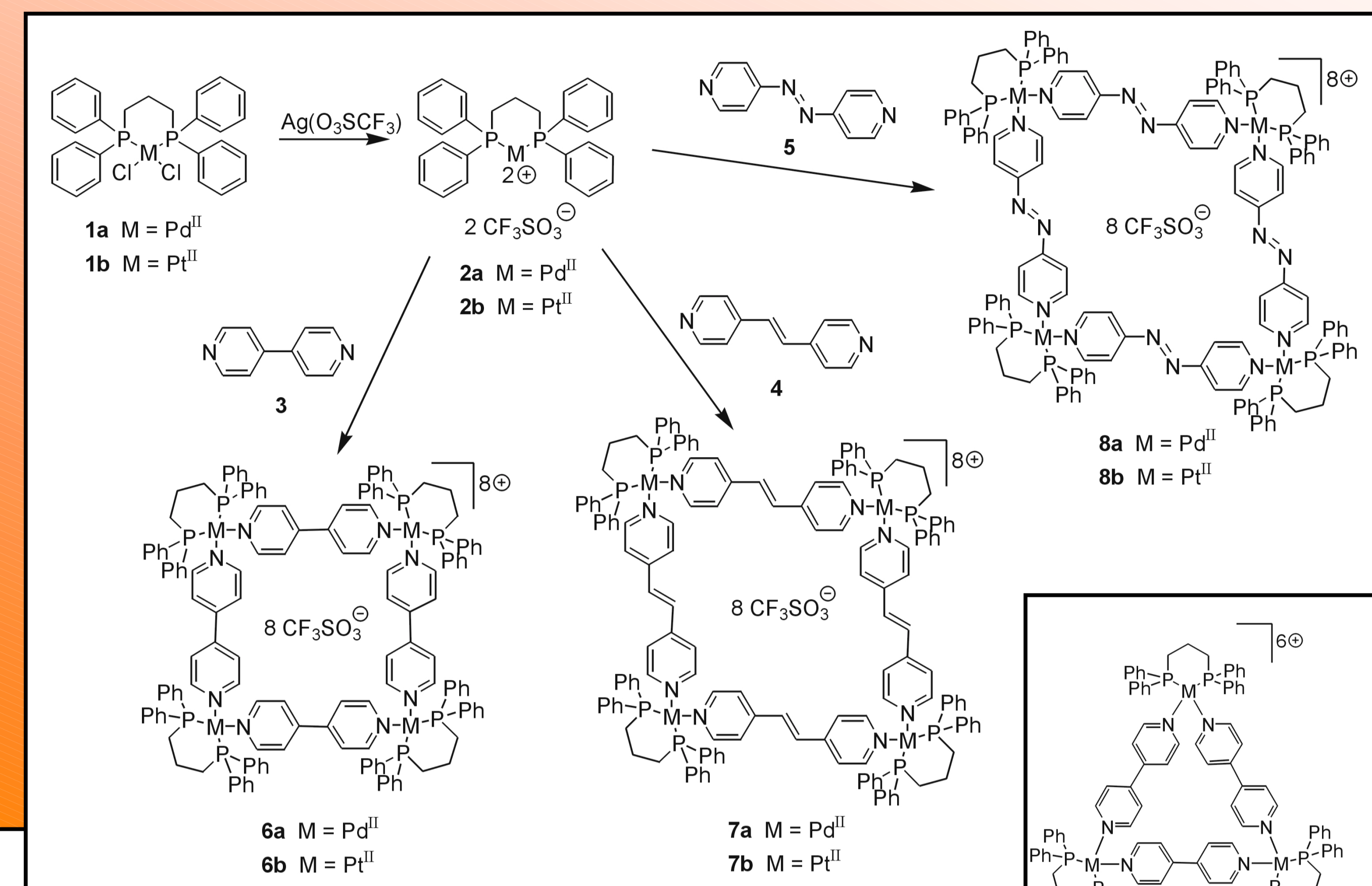


Mass Spectrometric Characterization and Gas-Phase Chemistry of Self-Assembling Supramolecular Squares

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I. Synthesis through Self-Assembly

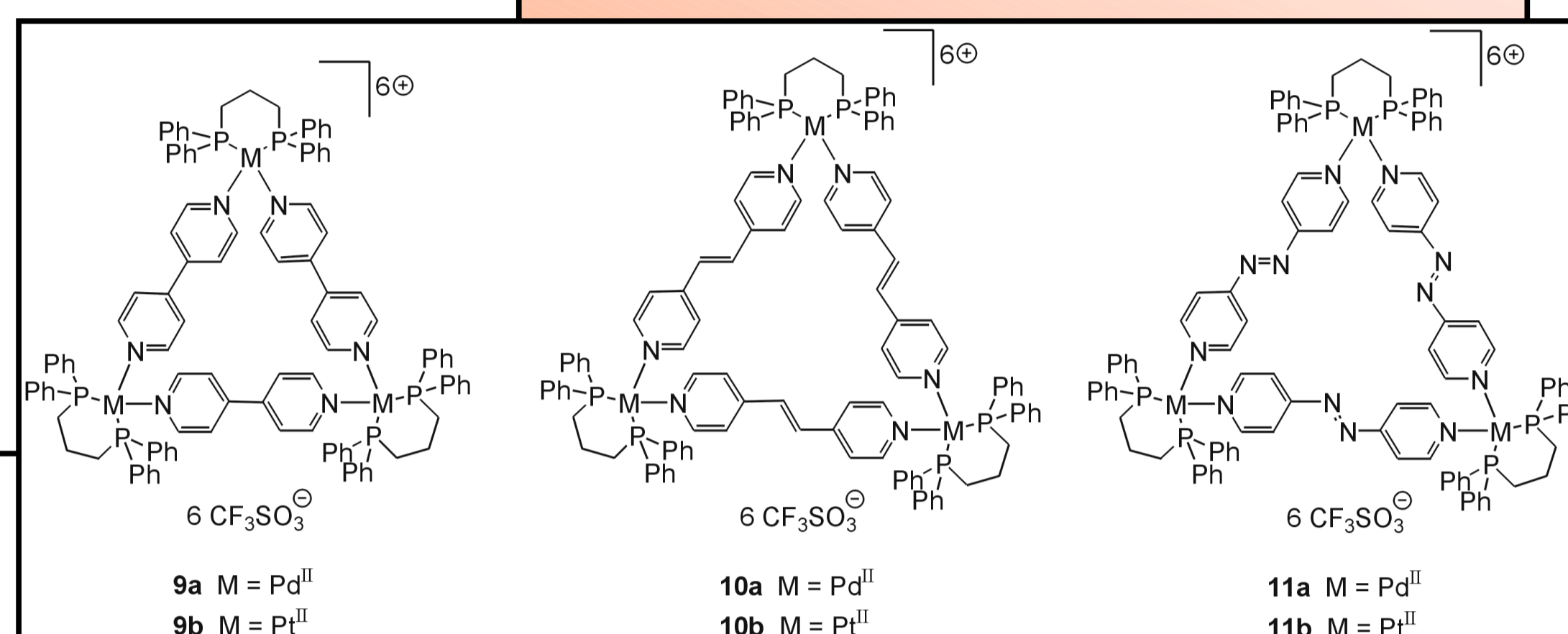


Supramolecular squares **6 – 8** can be self-assembled from simple building blocks avoiding the problems of covalent synthesis

Structural information must be written into the subunits by chemical synthesis (design of non-covalent interactions and rigidity)

Other assemblies might be possible (e.g. triangles **9 - 11**), thorough characterization mandatory

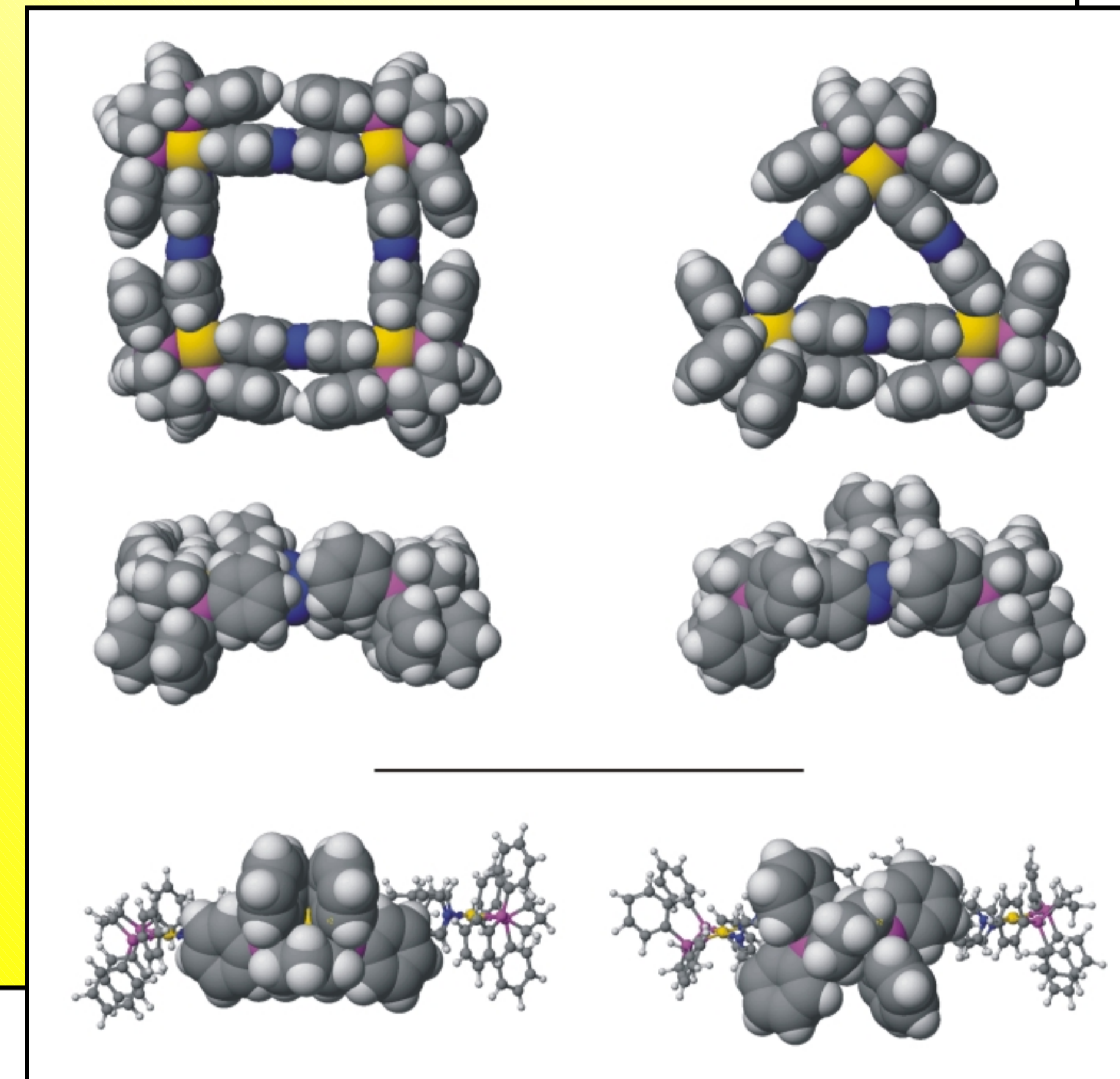
NMR characterization difficult due to high symmetry



II. Molecular Modeling

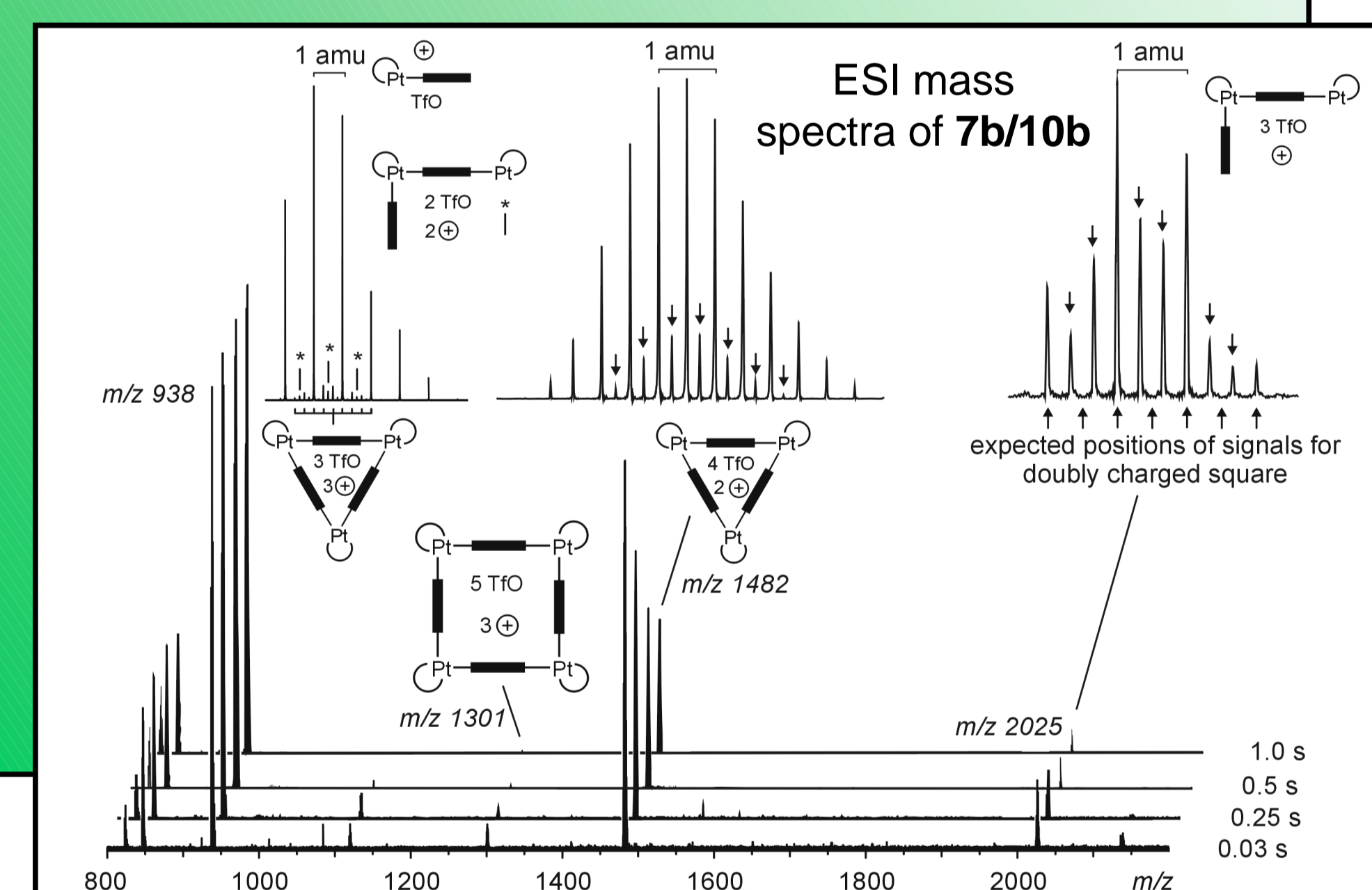
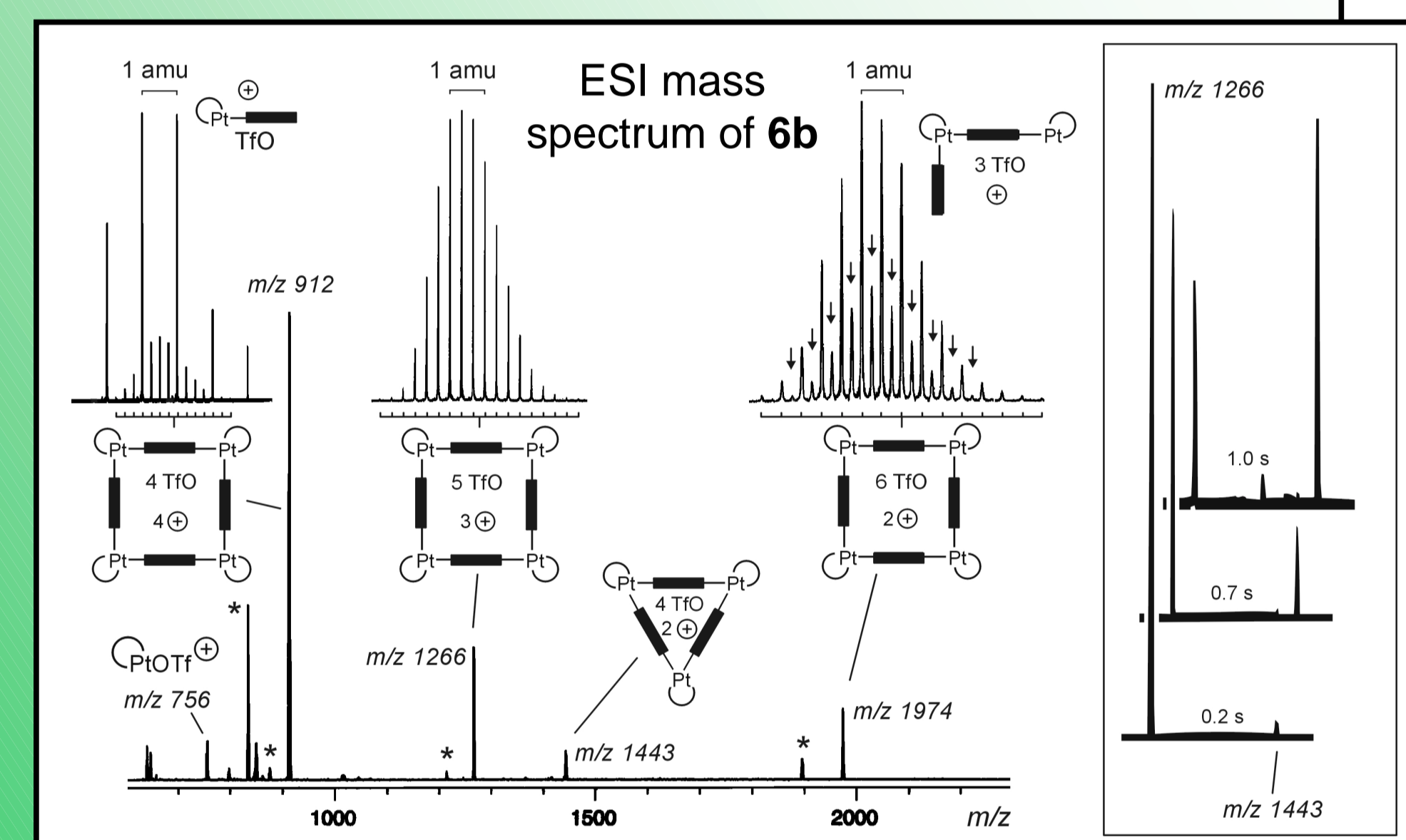
Molecular modeling results in low energy conformations with a stabilizing pyridine-phenyl stacking motif

Different conformations of the diphosphametallacyclohexane ring possible

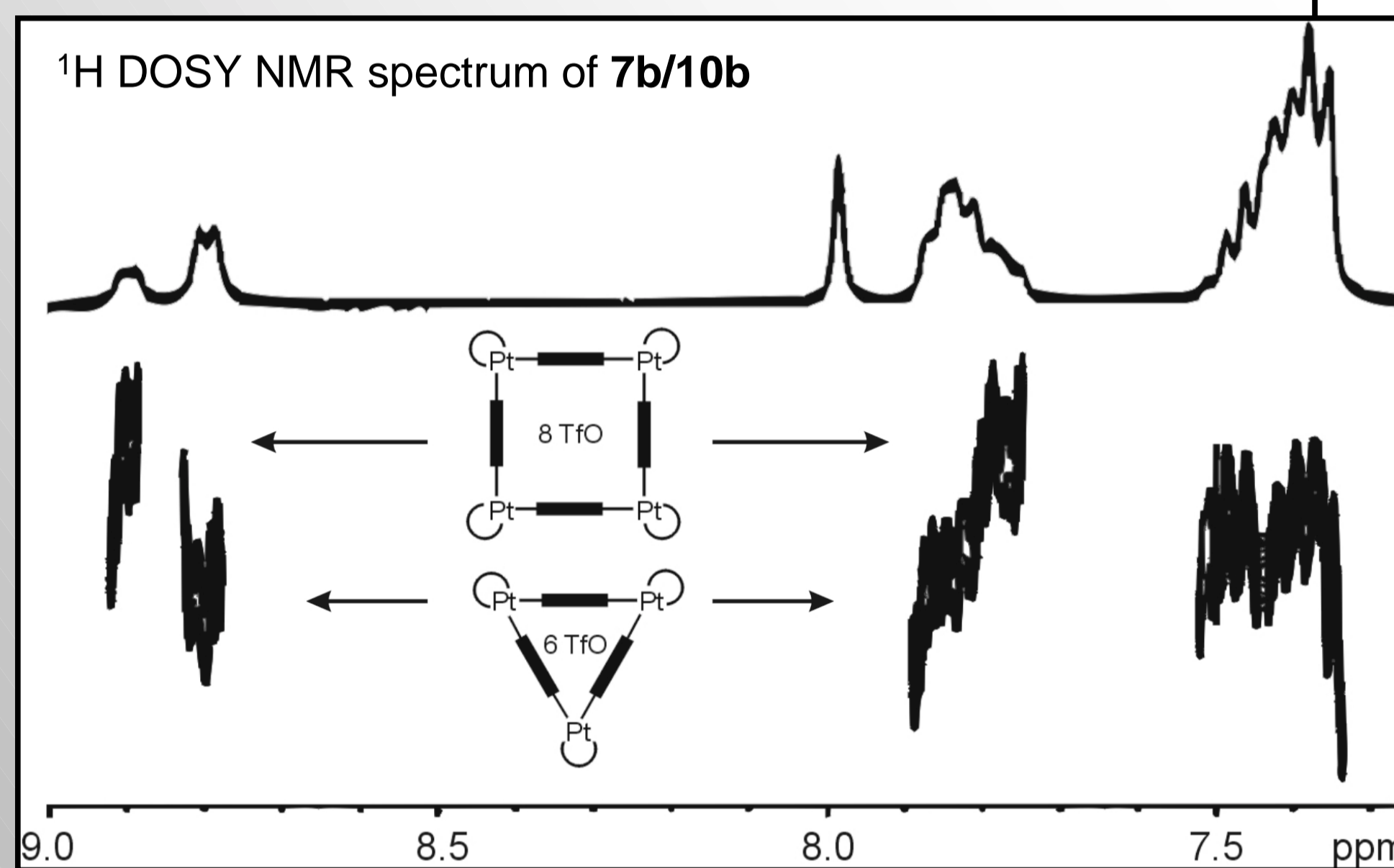


III. Characterization by ESI-FT-ICR Mass Spectrometry

Mass spectra indicate formation of triangles in solution for more flexible ligands **4** and **5** and formation of triangles in the gas phase by fragmentation of squares **6 - 8**



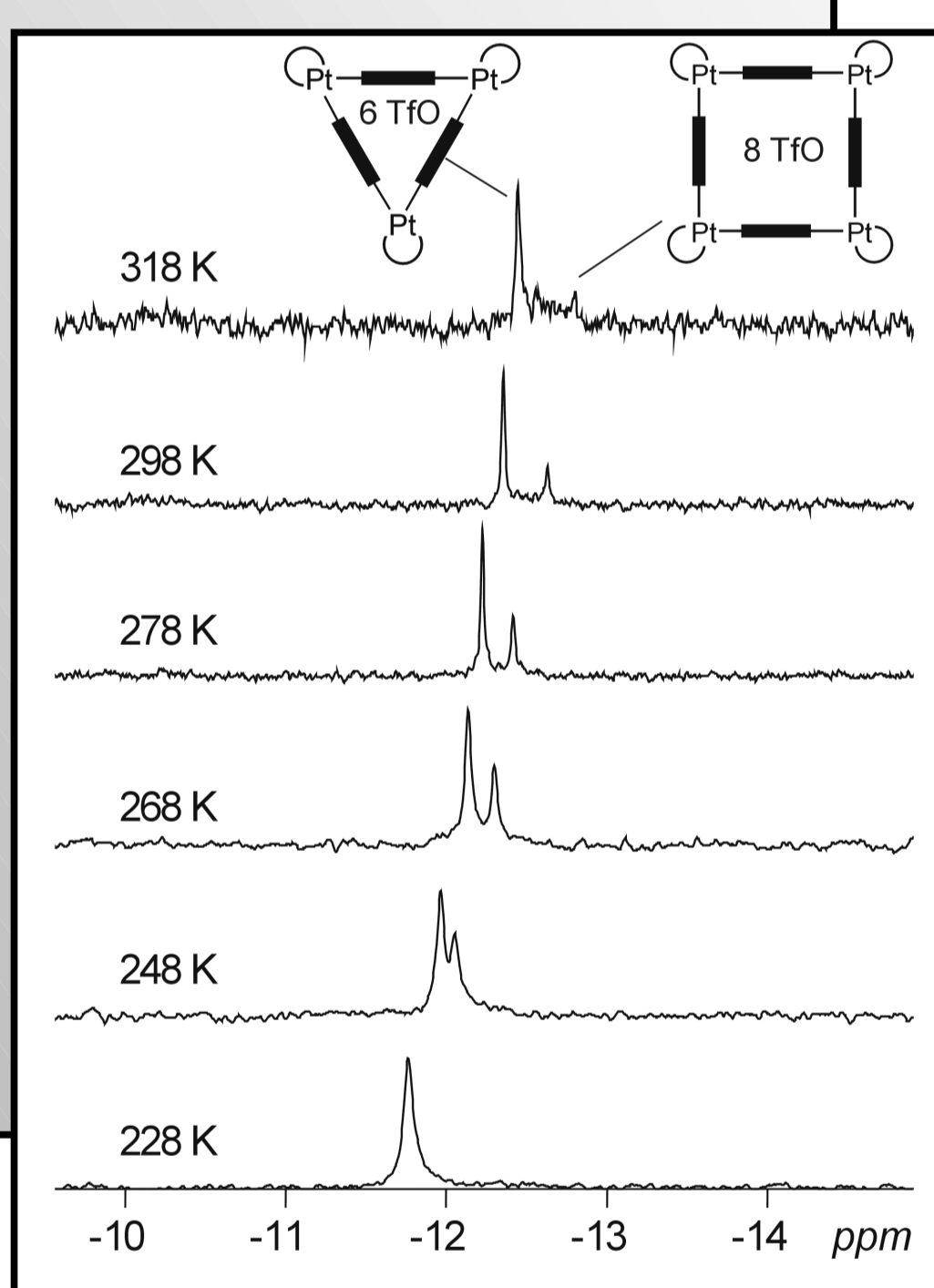
IV. NMR Spectroscopy



¹H, ³¹P, and DOSY NMR spectroscopy confirm the triangle-square equilibrium found by ESI-MS for **7a,b/10a,b** and **8a,b/11a,b**

Variable temperature ³¹P NMR spectra confirm shift of equilibrium towards triangles at higher temperatures

Triangles are enthalpically disfavored (strain), but entropically favored (larger number of particles)

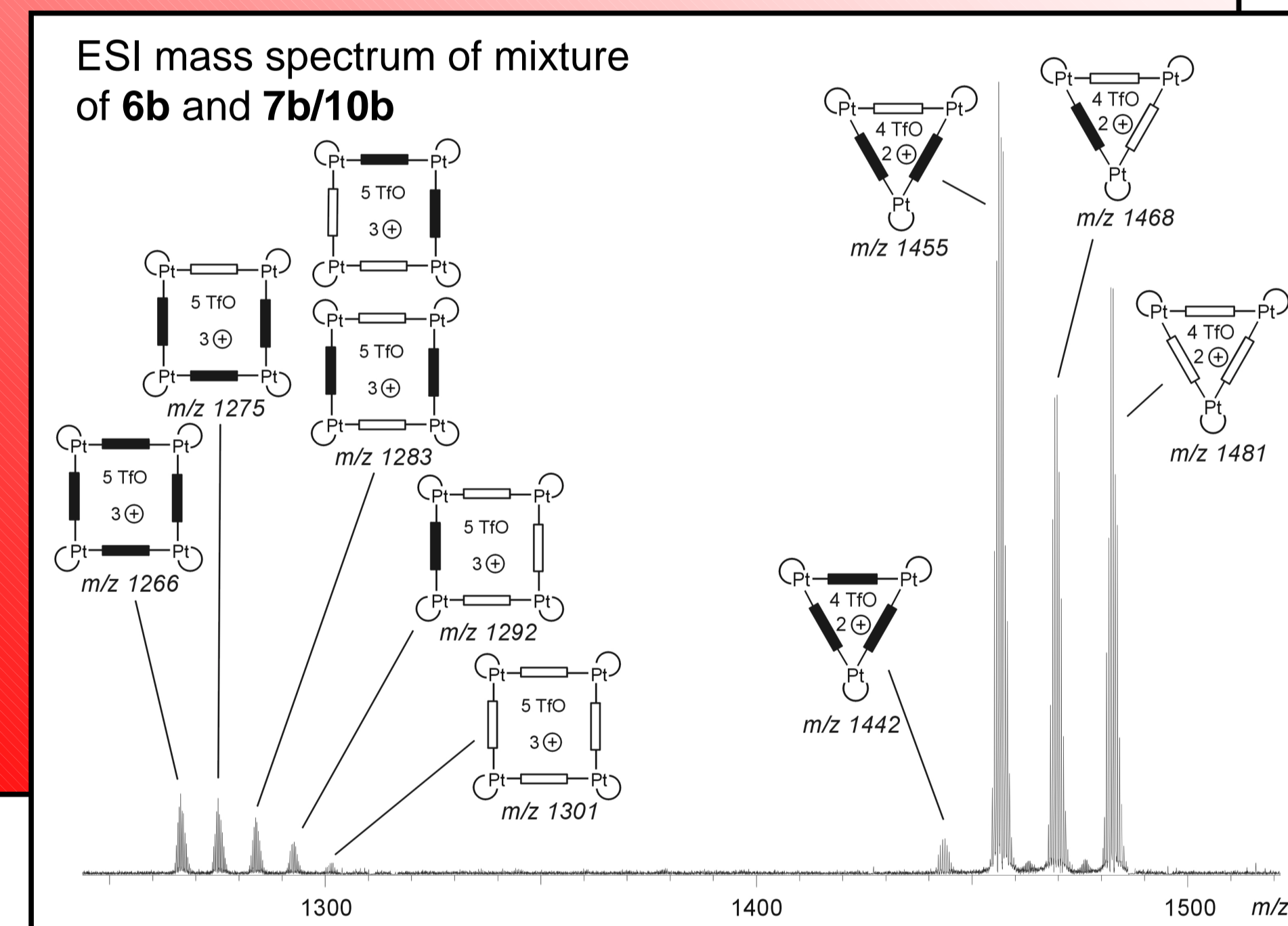


V. Ligand Exchange

While ligand exchange is fast (minutes) for palladium complexes, platinum squares exchange much more slowly (hours)

Ligand exchange confirmed by ³¹P NMR experiments; however complexity makes detailed analysis impossible

ESI mass spectra show formation of all possible triangles and squares



VI. Gas-Phase Chemistry: A Supramolecular „Neighbor Group“ Effect

Tandem-MS experiment performed with triply charged square (**6b-3TfO**)³⁺: Isolation of parent ion in the reaction cell of the FT-ICR mass spectrometer followed by Infrared Multiphoton Dissociation (IRMPD) with a CO₂ laser

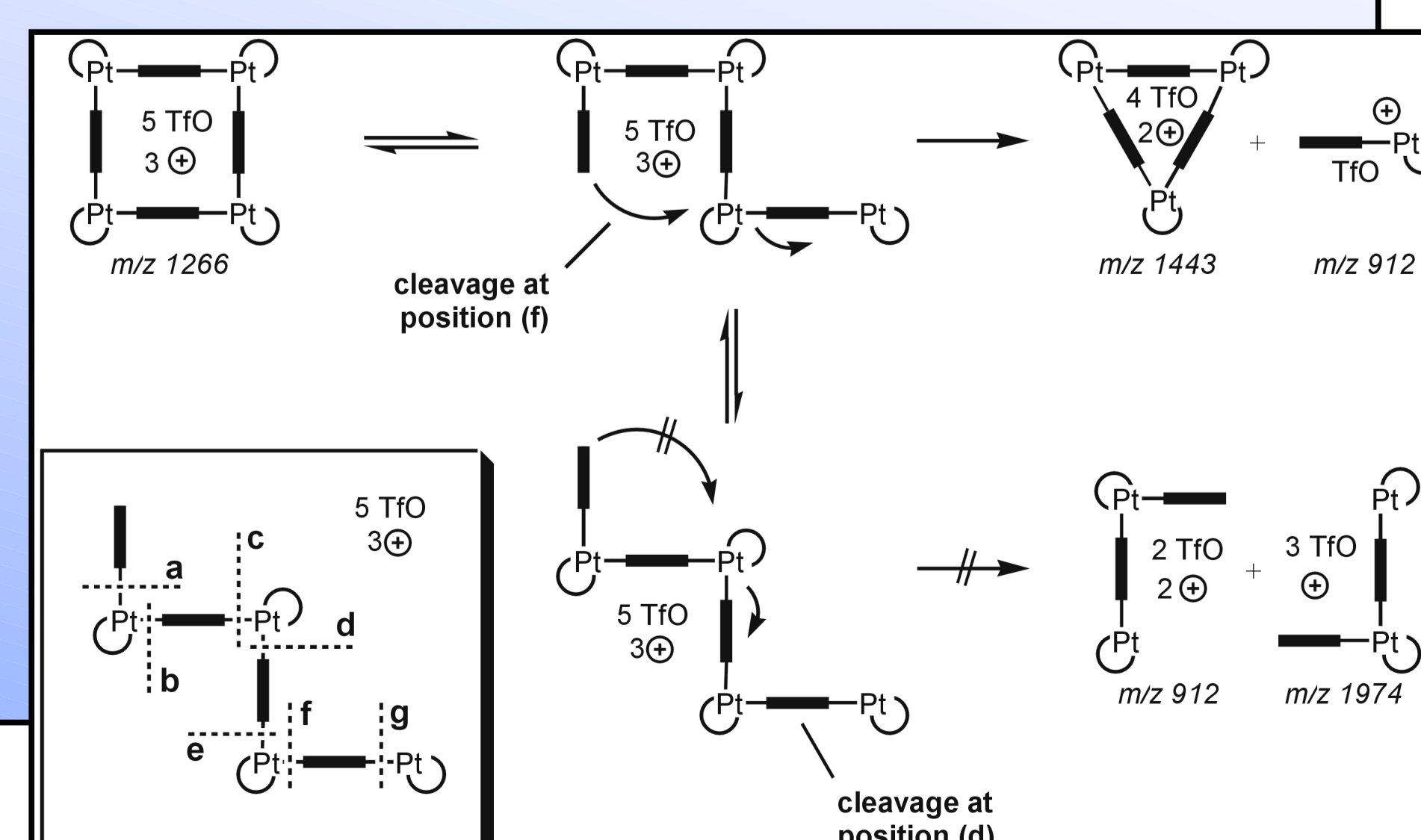
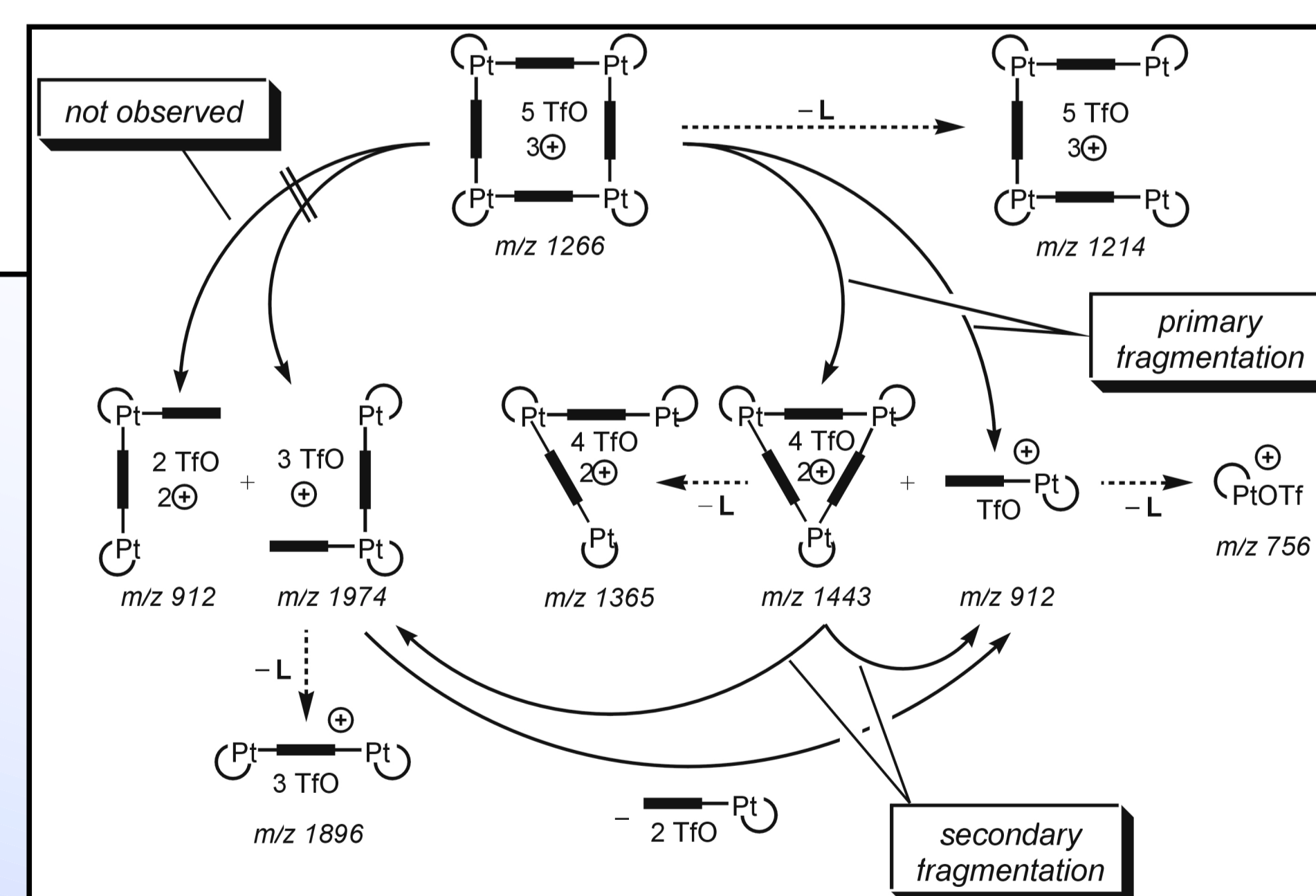
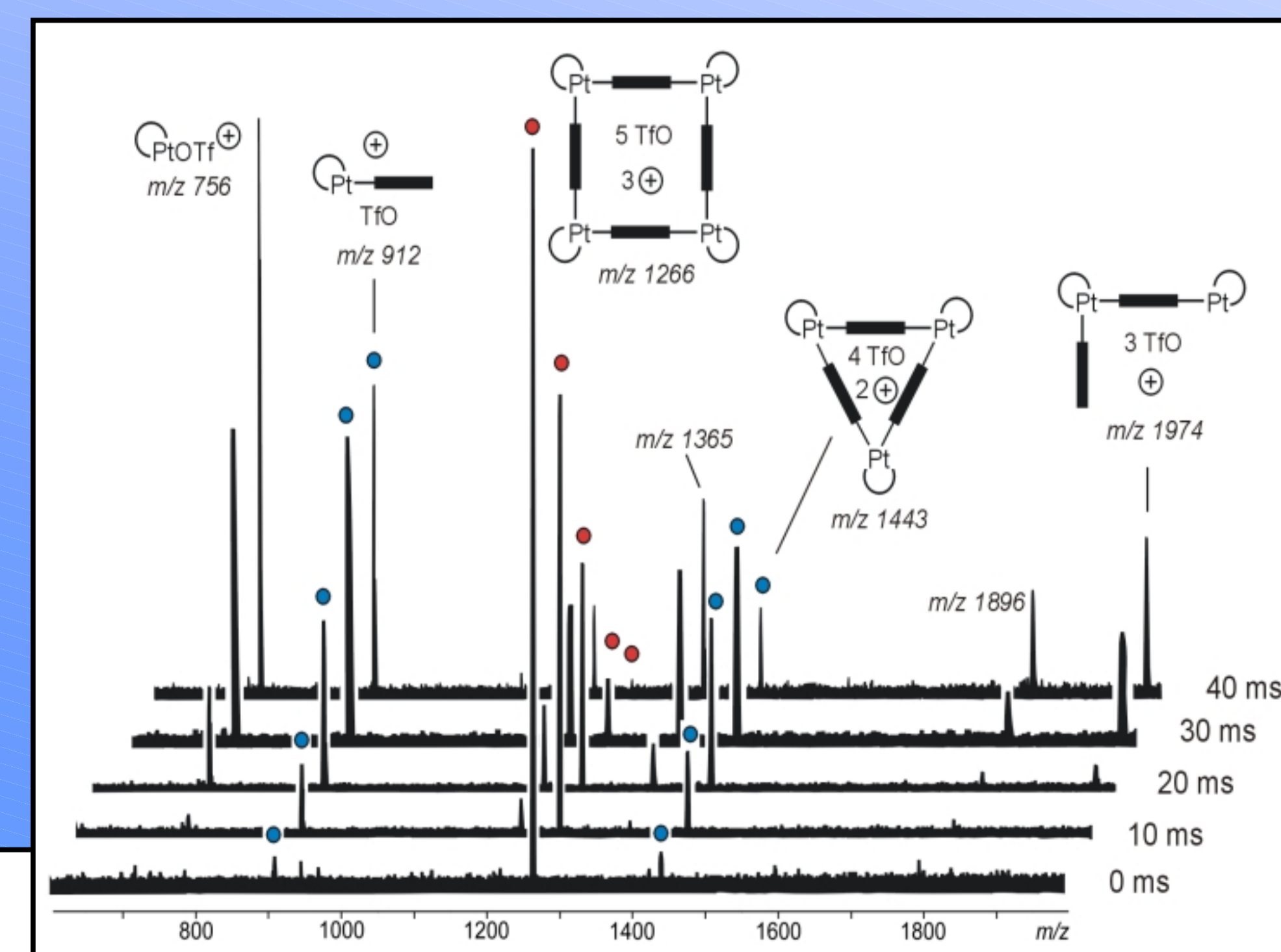
Fragmentation products can be kinetically followed over different irradiation times; primary and secondary products can be identified and monitored

One fragmentation reaction is strongly favored over others that should be energetically similar; [3+3] and [1+1] fragments are formed, while decomposition into two [2+2] fragments is not observed at all

Supramolecular equivalent of a neighbor group effect explains mechanistically the surprising preference for formation of [3+3] and [1+1] complexes

Consequently, triangle formation must be possible even from **6b**, although it is disfavored by some strain in solution and thus can only be observed in the gas phase

The strain energy must thus be lower than the binding energy of one Pt-N bond



Acknowledgment

We are grateful to Prof. Dr. Dietrich Gudat for measuring the DOSY-NMR spectrum. We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support.