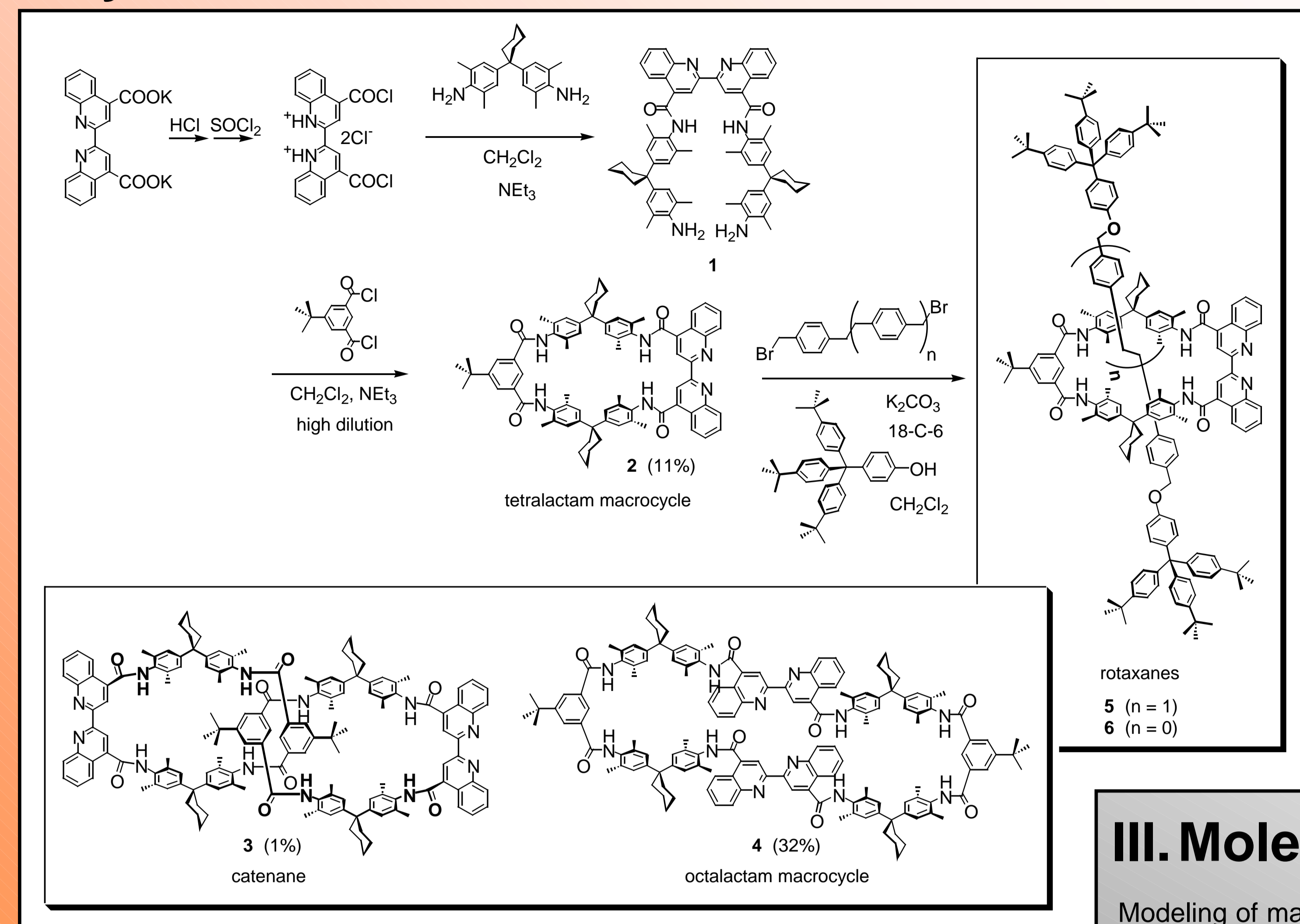


Macrocycles with Exocyclic Metal Binding Sites as Versatile Building Blocks for Supramolecular Chemistry

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I. Synthesis



New biquinoline-bearing tetralactam macrocycle 2 prepared together with the corresponding catenane 3 and octalactam macrocycle 4

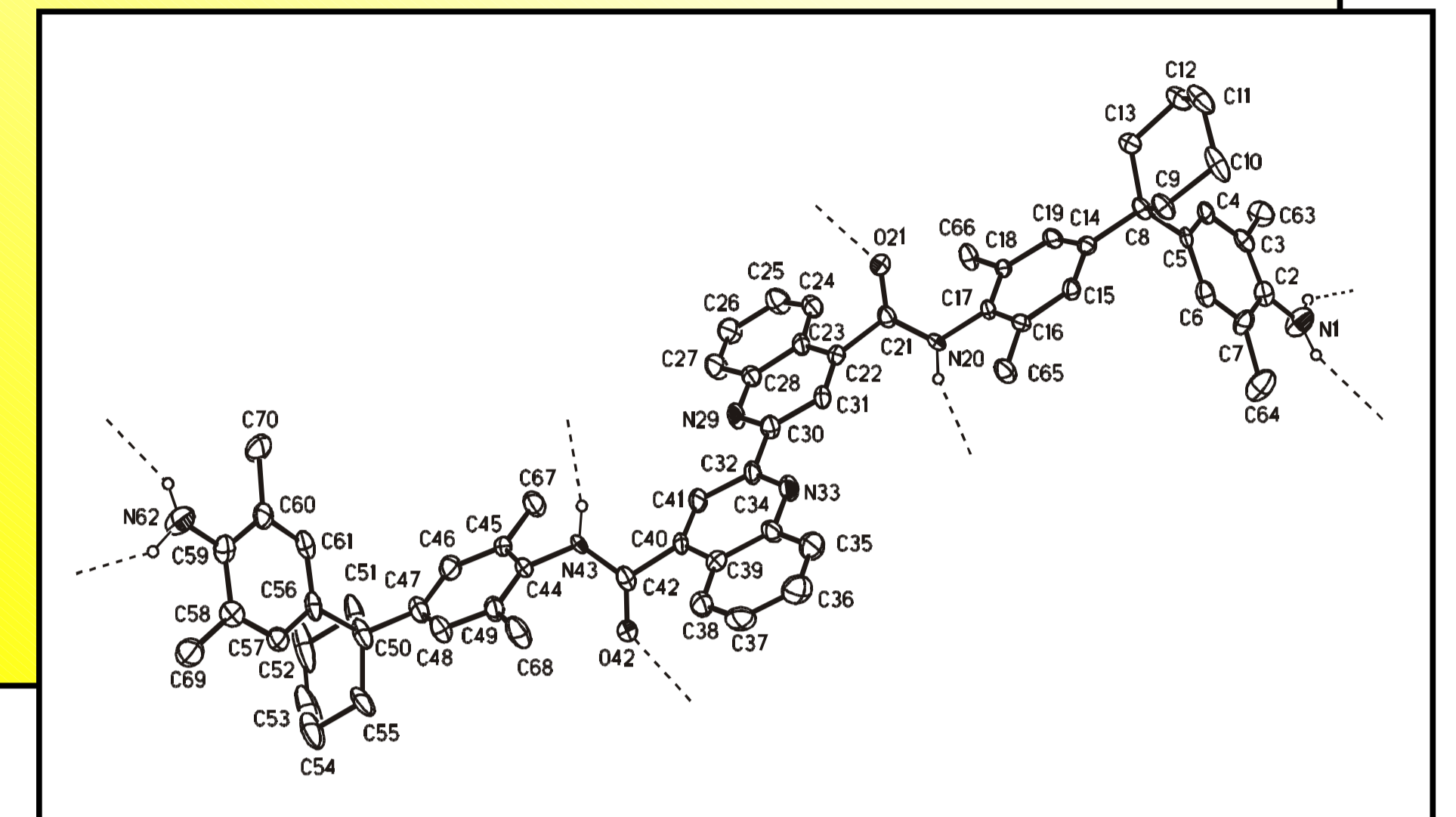
Larger, entropically less favorable octalactam 4 preferred due to transoid conformation of building block 1 (see X-ray single crystal structure)

Rotaxanes 5 and 6 can be made utilizing Vögtle's anion template effect with 25-35% yield

II. X-Ray Crystal Structure of 4

Building block 1 crystallizes from DMSO incorporating 7 DMSO molecules within the unit cell; DMSO is partially disordered

The preferred conformation is transoid with respect to the central biquinoline moiety (also confirmed by a 1000 step Monte Carlo conformational search)



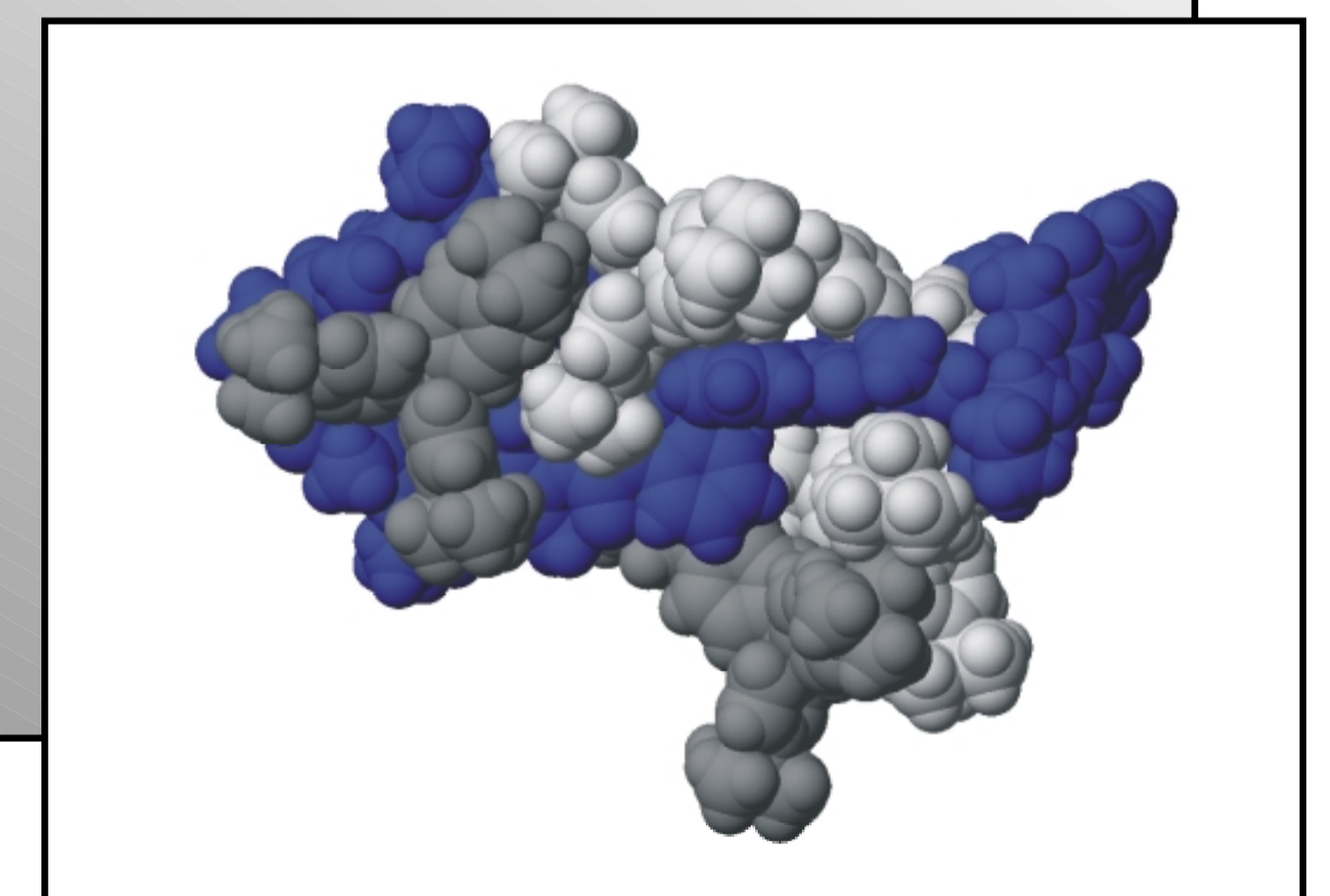
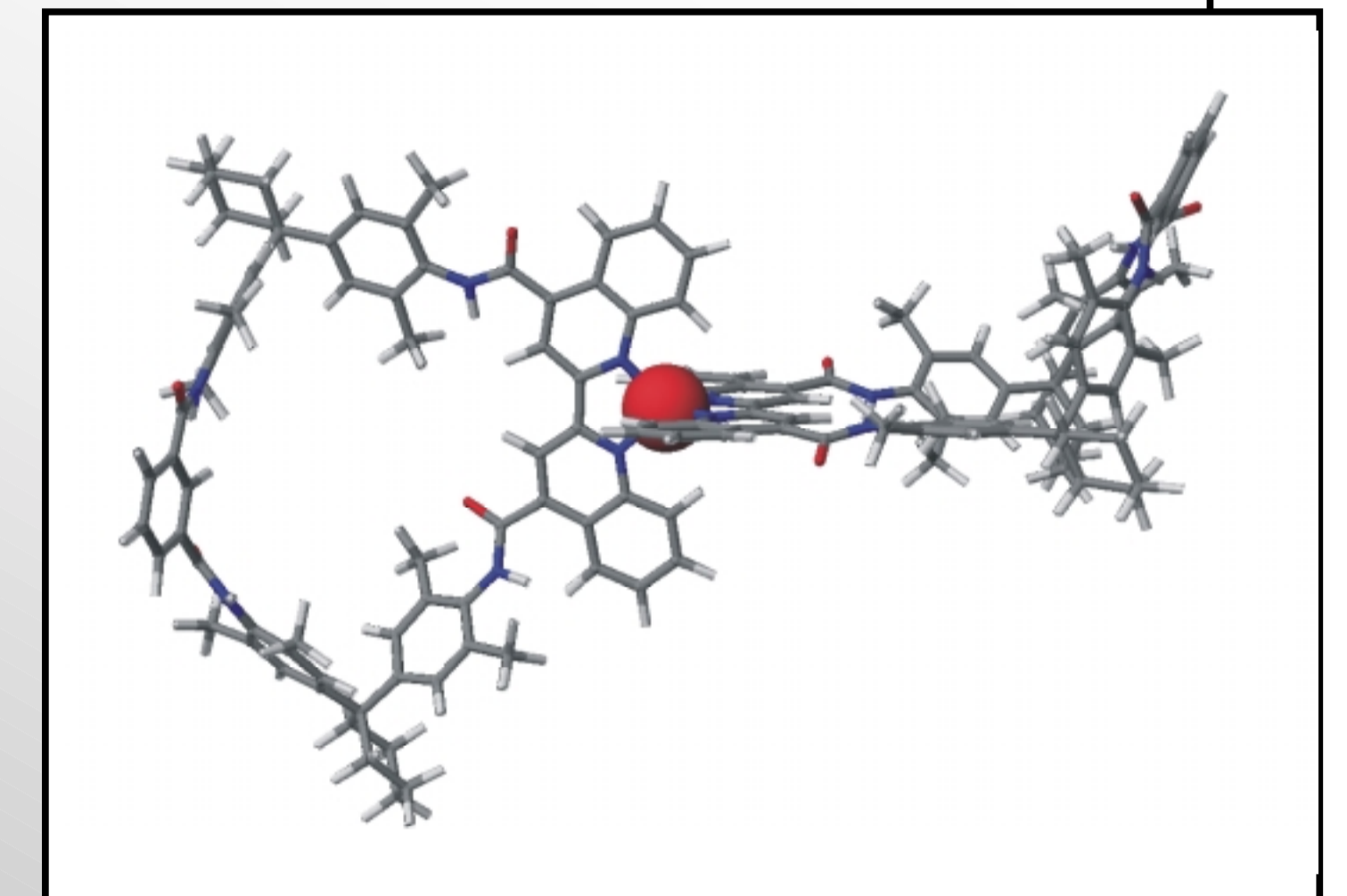
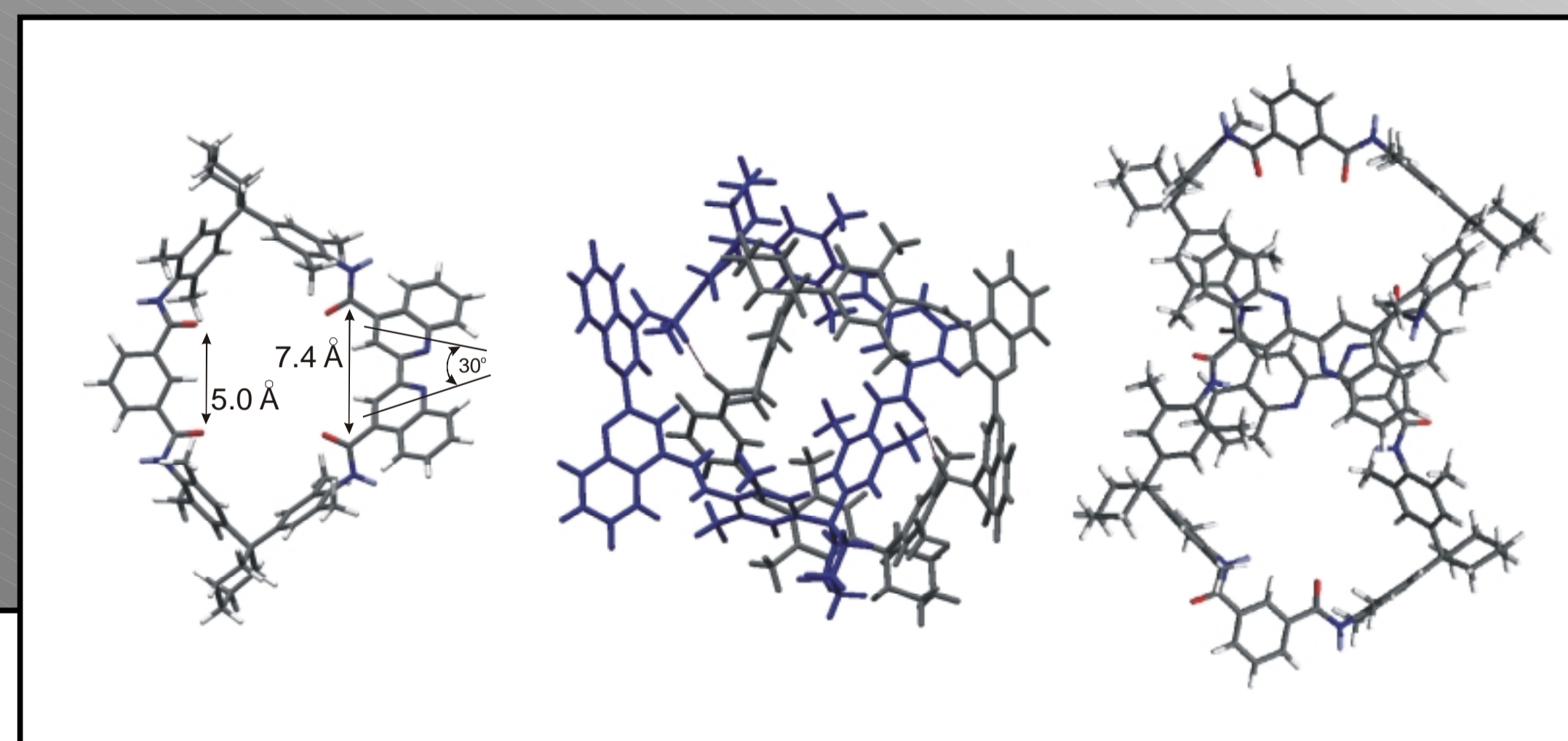
III. Molecular Modeling

Modeling of macrocycles 2 and 4 and the catenane 3 was carried out as 3000 step Monte Carlo conformational searches employing the AMBER* force field implemented in MacroModel 7.0

While 2 and 4 necessarily bear a cisoidal biquinoline, octalactam macrocycle 4 prefers a transoid conformation yielding an eight-shaped molecule

Cu(I) complexes were studied by molecular dynamics calculations with the augmented MM2 force field provided by the CACHE 5 program. Dynamics trajectories were run for 2 ns in steps of 2 fs at temperatures of 300 and 600 K

Most importantly, the tetrahedral ligand sphere around the Cu(I) center is more or less undistorted and not affected by introduction of the two rotaxane axes

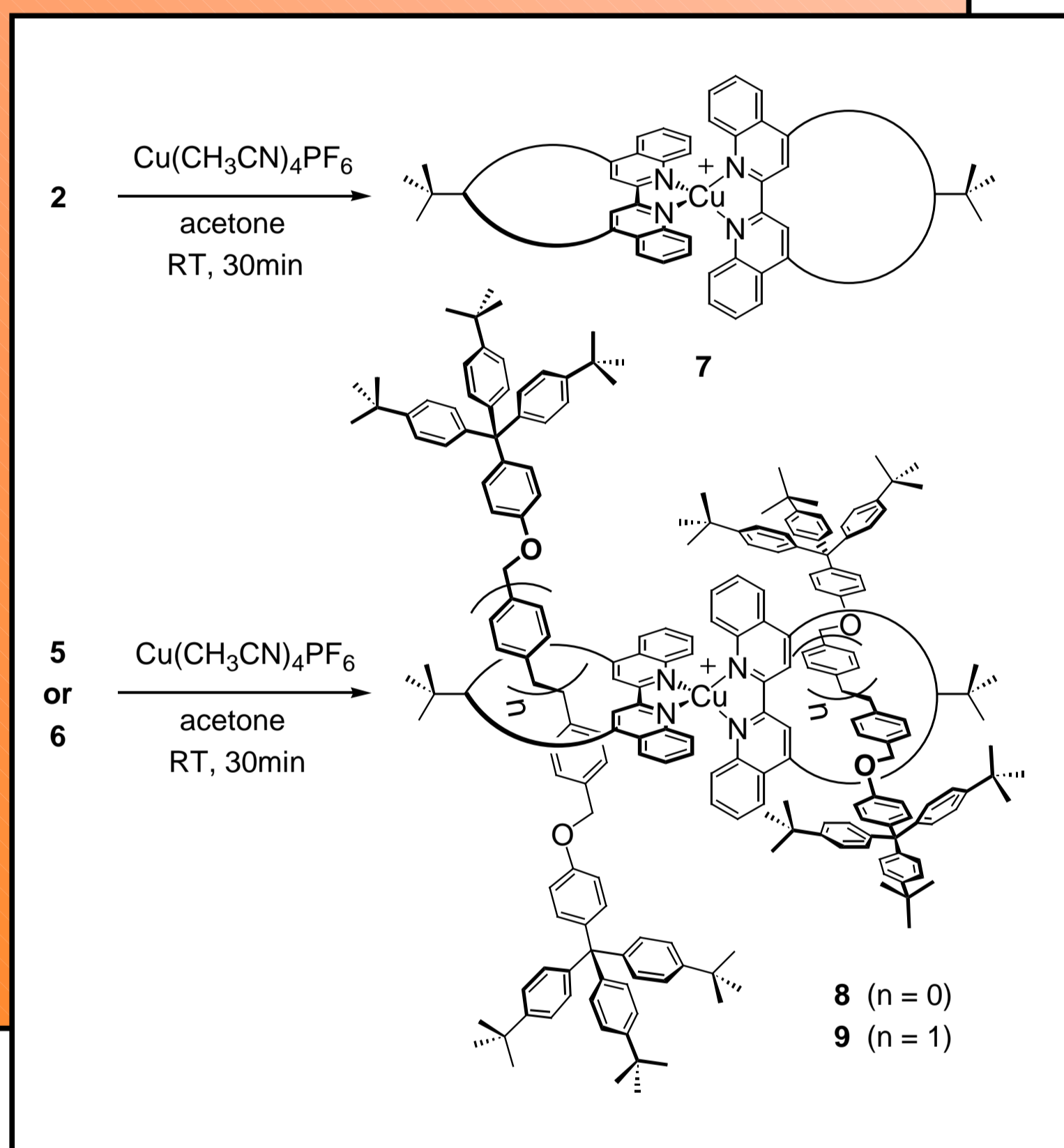


Due to the large size of the wheel, large stoppers are required; tris-(methylphenyl) methyl phenol stoppers do not work, neither do tritylphenols substituted with one or two methyl groups and two or one *t*-butyl groups

Macrocycle 2 and rotaxanes 5 and 6 dimerize through coordination to a Cu(I) ion in 50-75% isolated yield upon addition of Cu(CH₃CN)₄PF₆ in acetone

¹H NMR spectra confirm coordination to the Cu(I) ion by appropriate shifts of the biquinoline protons

MALDI mass spectrometry predominantly yields ions corresponding to [M-PF₆]⁺ and [M-Ligand-PF₆]⁺



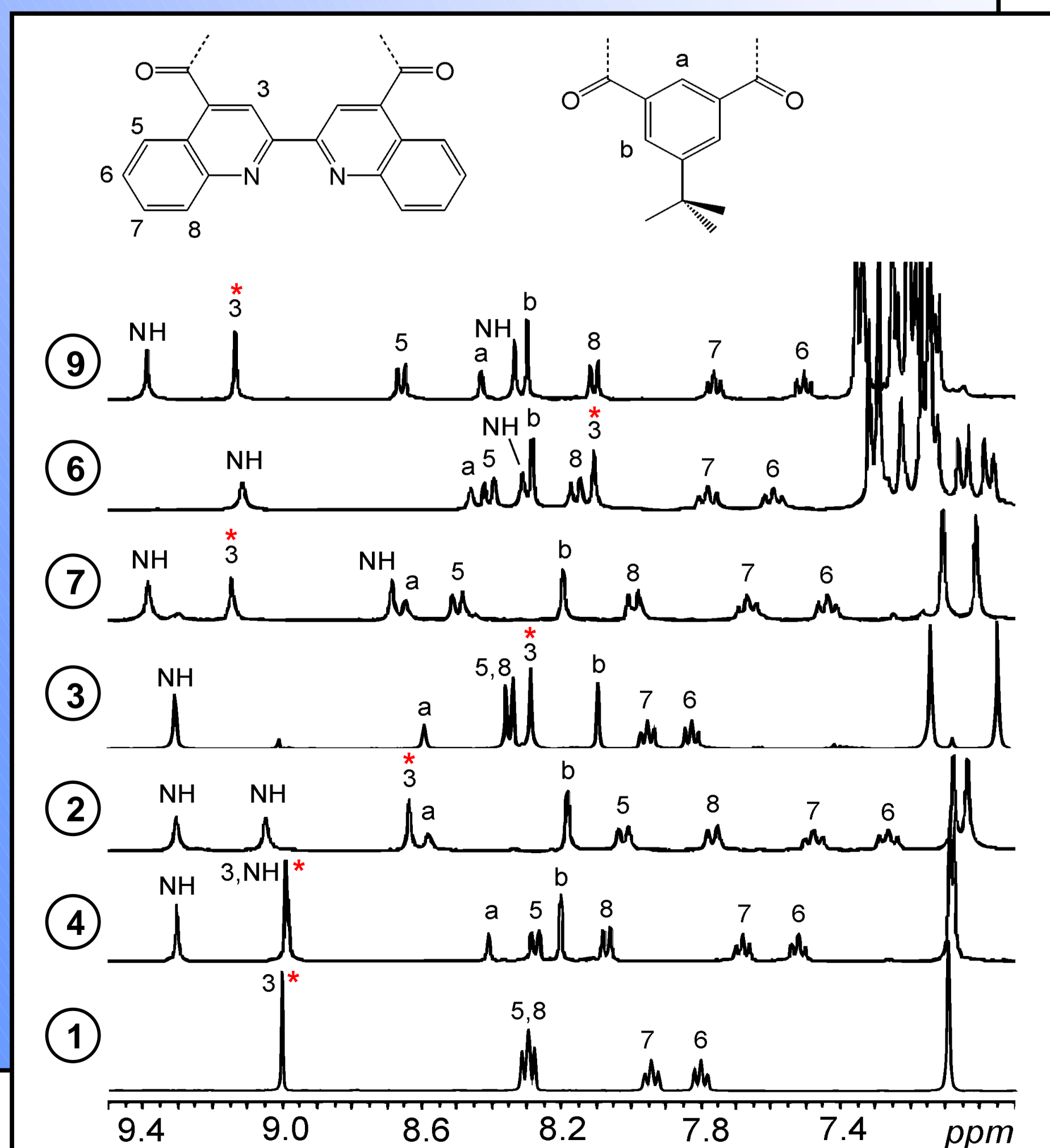
IV. NMR Spectroscopy

Signals for the 3,3' protons of the biquinoline subunits are particularly sensitive to the conformation of the biquinoline, the presence of an interlocked guest inside the cavity, and Cu(I) coordination

Building block 1 and macrocycle 4 prefer transoid conformation ($\delta(3,3') = 9.0$ ppm), macrocycle 2 is cisoid ($\delta(3,3') = 8.6$ ppm)

These protons experience an upfield shift in catenane 3 ($\delta(3,3') = 8.3$ ppm) and rotaxane 6 ($\delta(3,3') = 8.1$ ppm), while they appear at $\delta(3,3') = 8.6$ ppm in macrocycle 2

Upon Cu(I) coordination they shift downfield to $\delta(3,3') = 9.2$ ppm

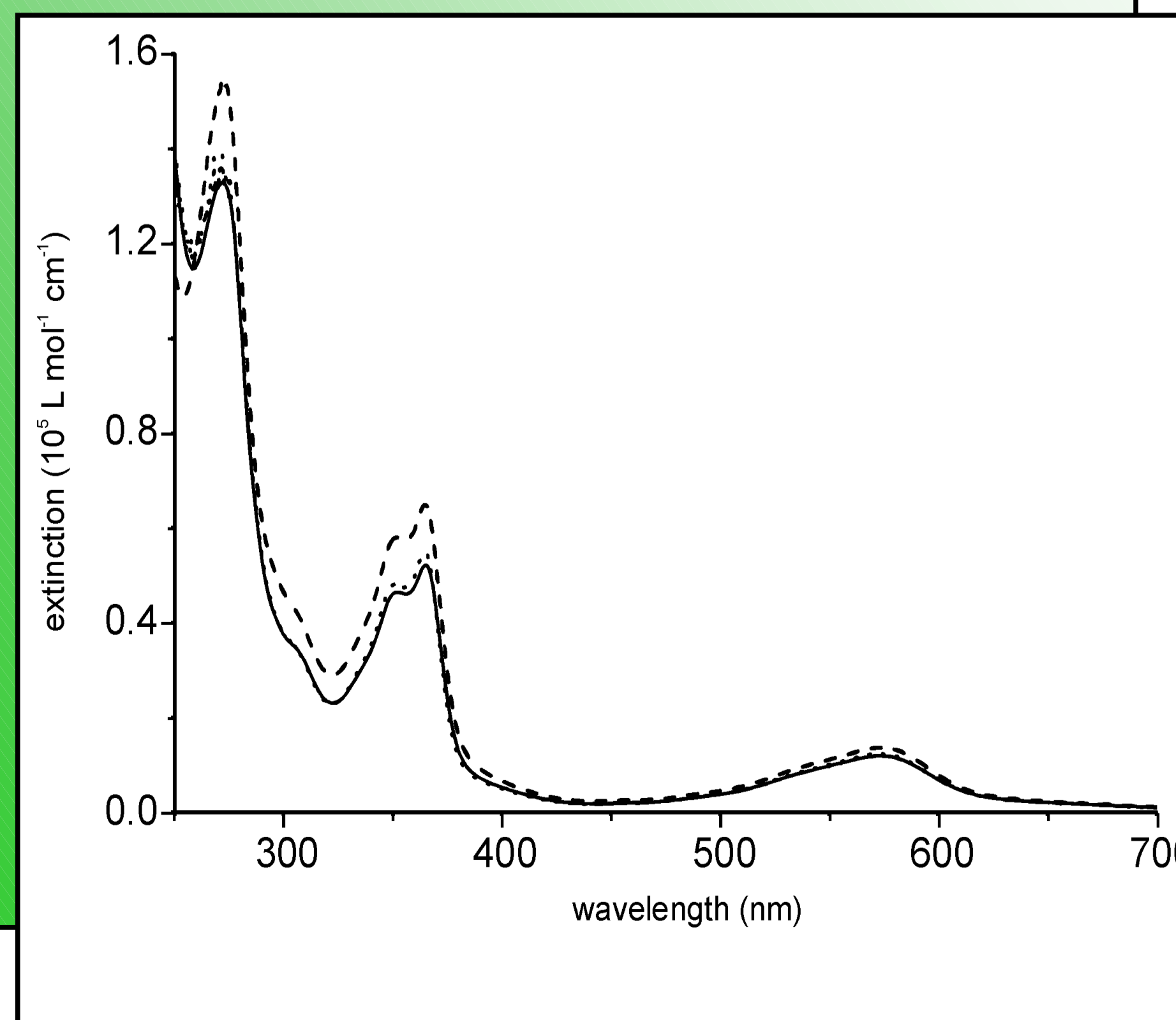


V. UV/VIS Spectroscopy

In the UV/VIS absorption spectra of 7, 8, and 9 bands in the range of 250 to 400 nm likely correspond to $\pi-\pi^*$ transitions, while an MLCT band appears at 574 nm

The MLCT band is red-shifted by ca. 30 nm against the band of a simple bis-(biquinoline) copper complex, probably due to substitution with amide groups

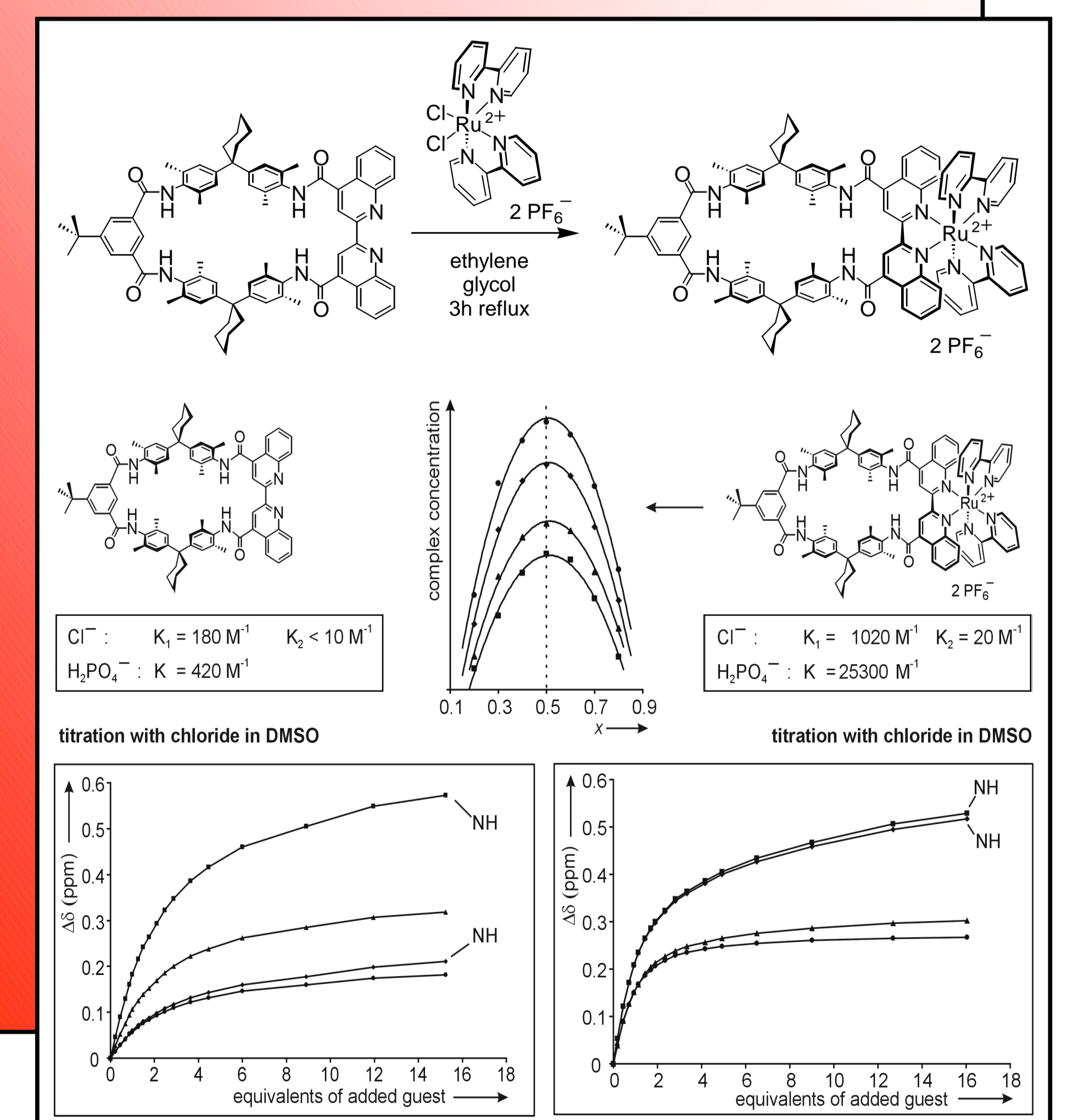
The high similarity between the three spectra of 7, 8, and 9 indicates in good agreement with molecular modeling results that introduction of the axle and its nature does not affect the ligand sphere around the central copper ion



VI. Anion Binding to Ru complex

A bpy₂Ru(II) complex of macrocycle 2 was prepared and compared to free 2 with respect to its anion binding behavior (Job plots, NMR titrations)

Enhanced binding to the metal complex in DMSO and a preference for dihydrogen phosphate over chloride are observed



Acknowledgment

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