

Syntheses of 2,2'-Bipyridin-6-carbaldehydes for Transition Metal Complexes with tunable N6-Donor Set

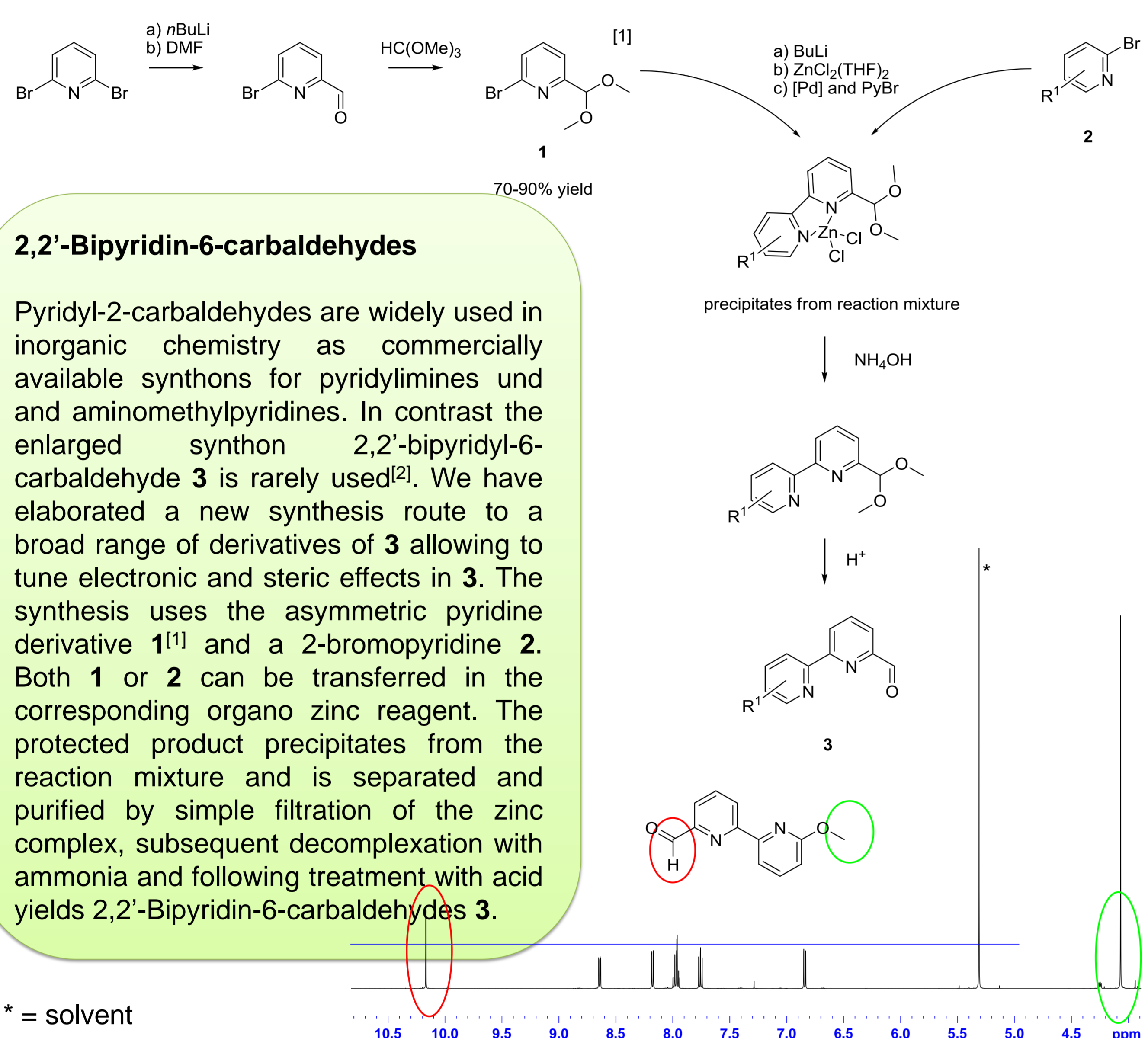
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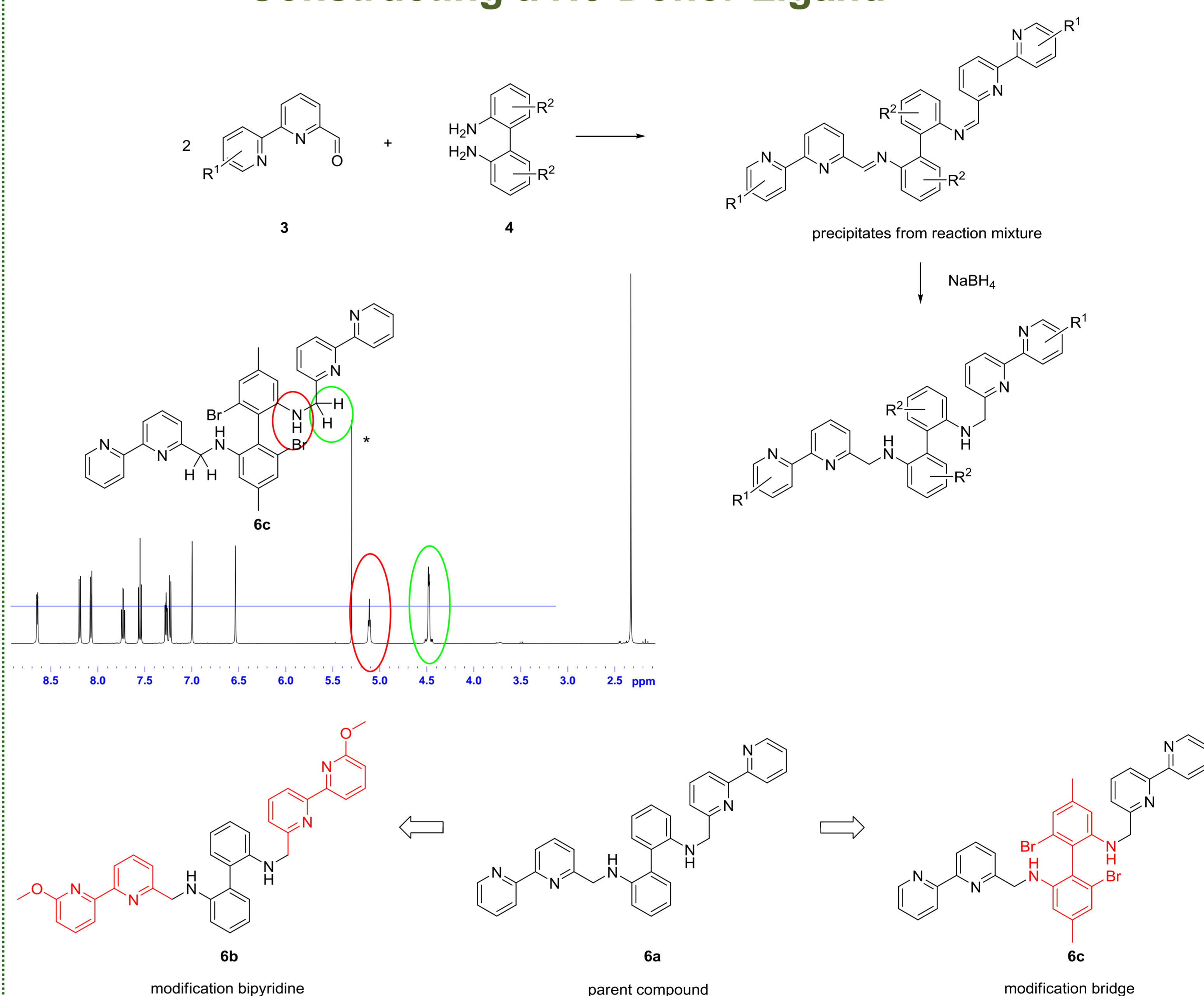
Introduction

Transition metal complexes have unique properties due to their open d shell. To make use of them in new materials for data storage, for sensors or new displaying technologies precise tuning of the ligand field strength is essential. Among the vast amount of described ligands in transition metal complexes the good π -acceptor polypyridyl ligands like 2,2'-bipyridine and 2,2';6',2''-terpyridine derivatives are among the most popular, however, synthesis of those ligands is still a challenge. We have used Negishi cross coupling to obtain 2,2'-bipyridyl-6-aldehydes **3** using the easily available asymmetric pyridine derivative **1**^[1]. The high yield in the Negishi cross coupling allows the efficient introduction of the second pyridine **2** in a late step of the synthesis. Aldehydes **3** have been employed in the synthesis of polypyridylamines **5**. The tuning of ligand field in the transition metals complexes employing **5** as ligands was demonstrated on Fe²⁺ spin crossover (SCO) complexes **6**.

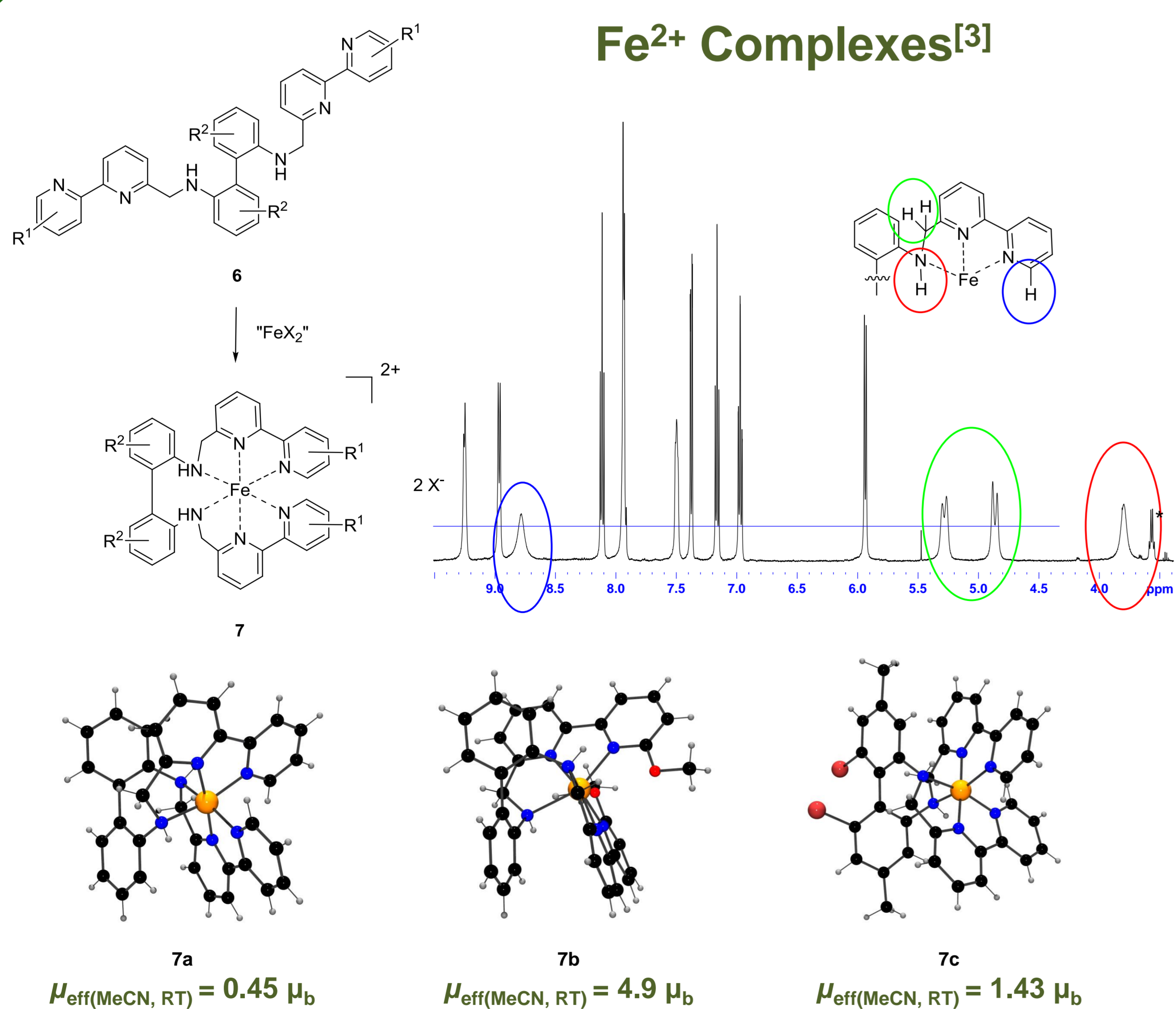
Synthesis of 2,2'-Bipyridyl-6-Aldehydes



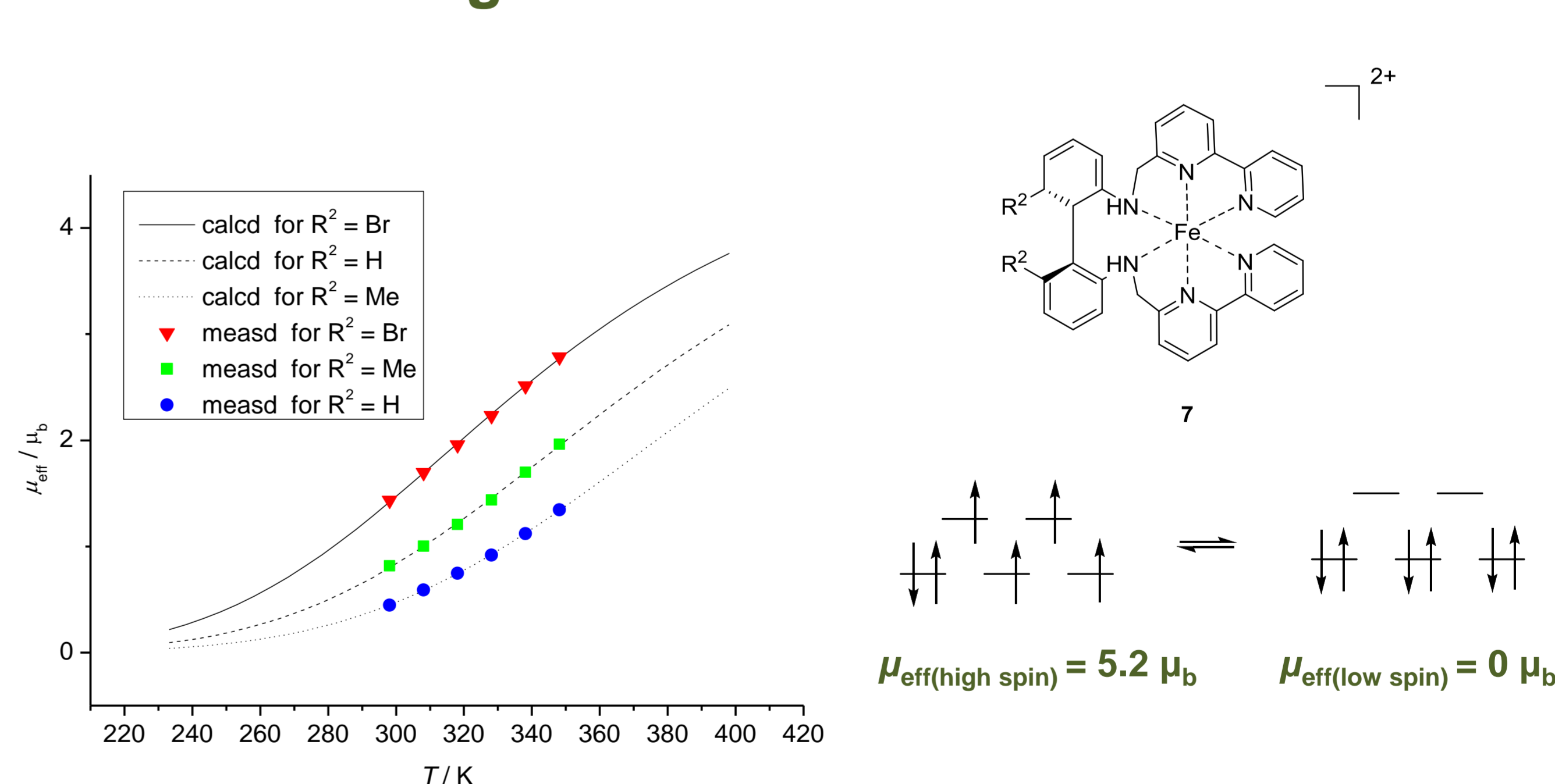
Constructing a N6-Donor Ligand



Fe²⁺ Complexes^[3]



Tuning of SCO Transition^[3]



For Fe²⁺ complexes **7a** (R² = H), **7c** (R² = Br) and **7d** (R² = Me) the magnetic moment was determined in MeCN solution using Evans' method. The measured data was fitted to a regular solution model yielding the ΔH , $T_{1/2}$ and subsequently ΔS . For all complexes ΔS was calculated to about 56 J/mol·K, significant different is ΔH (19.1 kJ/mol (**7d**), 20.6 kJ/mol (**7c**) and 22.5 kJ/mol (**7a**)). A correlation between torsion of the biphenyl bridge in solid state and $T_{1/2}$ is found.

Conclusion

In summary, we have used 2,2'-bipyridin-6-carbaldehydes **3** for the synthesis of polypyridylamines **6**, that are employed as ligands in Fe²⁺ spin crossover complexes. The used bridge **4** allows the direct tuning of the spin transition temperature $T_{1/2}$ in the SCO complexes by steric effects.^[3]

References

- [1] R. G. Hicks, B. D. Koivisto, M. T. Lemaire, *Org. Lett.* **2004**, *6*, 1887-1890.
- [2] a) E. C. Constable, G. Zhang, C. E. Housecroft, M. Neuburger, S. Schaffner, *Dalton Trans.* **2009**, 8165-8167; b) L. J. Baird, C. A. Black, A. G. Blackman, *Polyhedron* **2007**, *26*, 378-384; c) E. C. Constable, G. Zhang, C. E. Housecroft, M. Neuburger, J. A. Zampese *Eur. J. Inorg. Chem.* **2010**, 2000-2011; d) E. C. Constable, G. Zhang, C. E. Housecroft, M. Neuburger, J. A. Zampese *Chem. Commun.* **2010**, 3077-3079; E. C. Constable, G. Zhang, C. E. Housecroft, J. A. Zampese *Dalton Trans.* **2010**, 5332-5340.
- [3] H. Petzold, S. Heider submitted.

Acknowledgement

We are grateful to the Fonds der Chemischen Industrie for a Liebig Stipendium (H.P.).

