Synthesis of Transition Metal Complexes with Tuneable N6-Coordination Sphere

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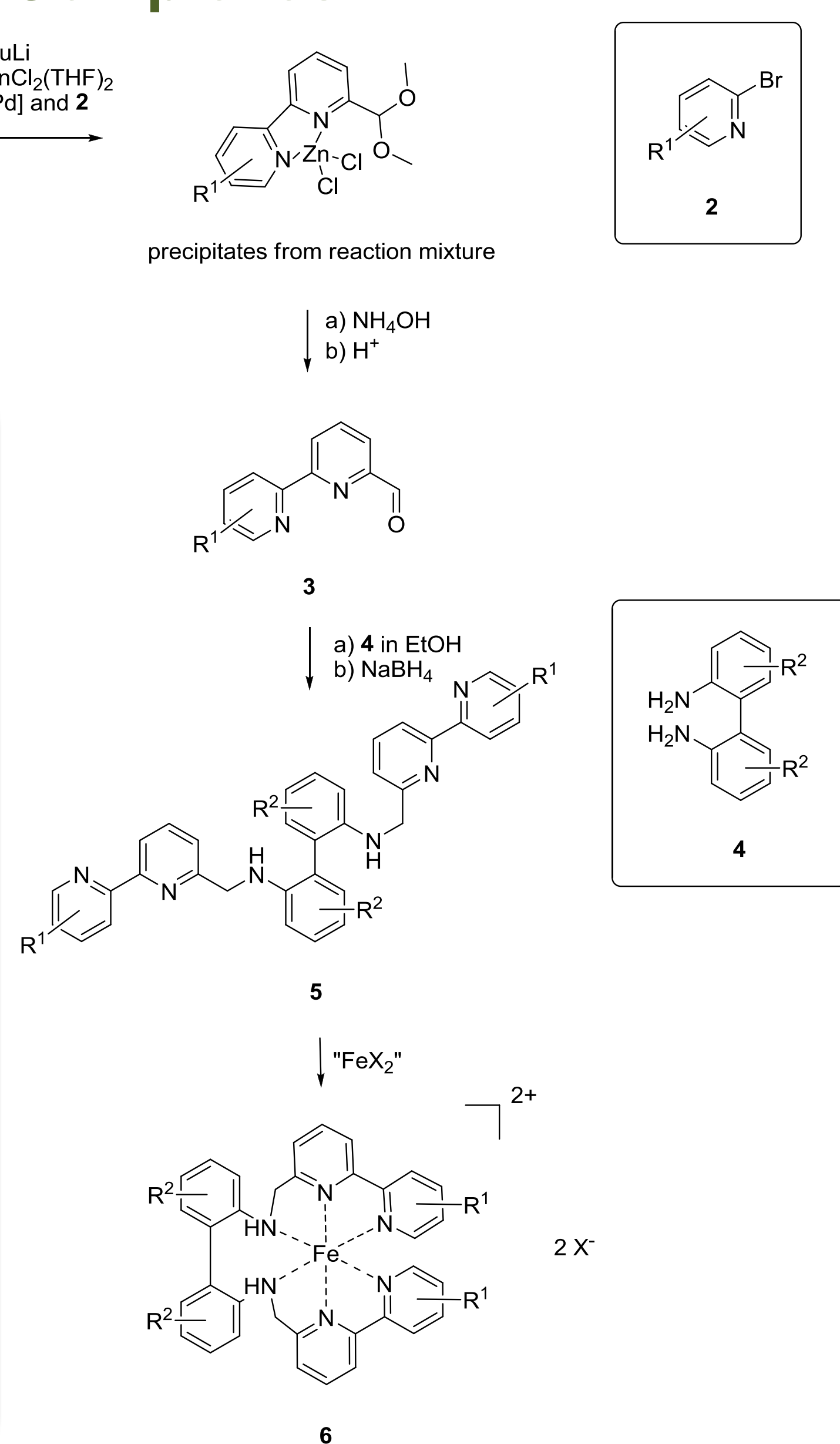Dr. Holm Petzold; phone: +49(0)371 531 37463, email: holm.petzold@chemie.tu-chemnitz.de

Introduction

Transition metal complexes have unique properties due to their open d shell. To make use of them in new materials for data storage, 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 polypridyl 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 4 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 ring from a bromopyridine 2 in a late step of the synthesis. Aldehydes 3 have been employed in the synthesis of polypyridylamines 5.[3] The tuning of the ligand field strength in the transition metal complexes employing 5 as ligands was demonstrated on Fe^{2+} spin crossover (SCO) complexes 6. Using Aldehydes 3 and di-, tri- or tetraaminoaryl derivatives allows the expansion to polynuclear complexes with interacting Fe^{2+} SCO centers.

Construction of the N6-Donor Ligand Scaffold for Fe²⁺ Complexes[3]

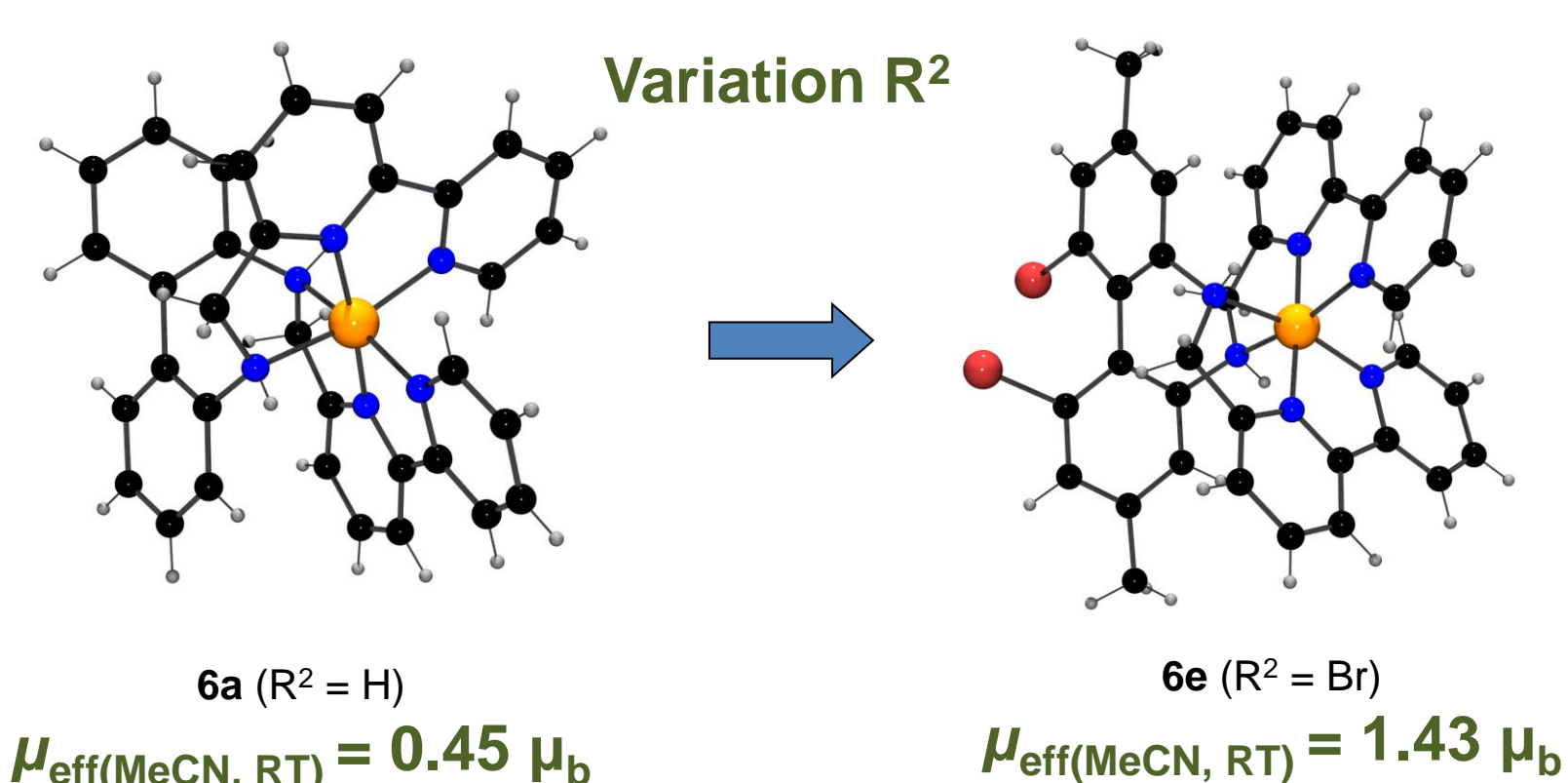### 2,2'-Bipyridin-6-carbaldehydes

Pyridyl-2-carbaldehydes are widely used in inorganic chemistry as commercially available synthons for pyridylimines and aminomethyl-pyridines. In contrast the enlarged synthon 2,2'-bipyridyl-6-carbaldehyde 3 is rarely used.[2] We have elaborated a new synthesic route to a broad range of derivatives of 3 allowing to tune electronic and steric effects in 3. The synthesis uses the asymmetric pyridine derivative 1[1] and a 2-bromopyridine 2. Both 1 or 2 can be converted into the corresponding organo zinc reagent. The protected product precipitates from the reaction mixture and is separated and purified by simple filtration of the zinc complex. Subsequent decomplexation with ammonia and following treatment with acid yields 2,2'-bipyridin-6-carbaldehydes 3.
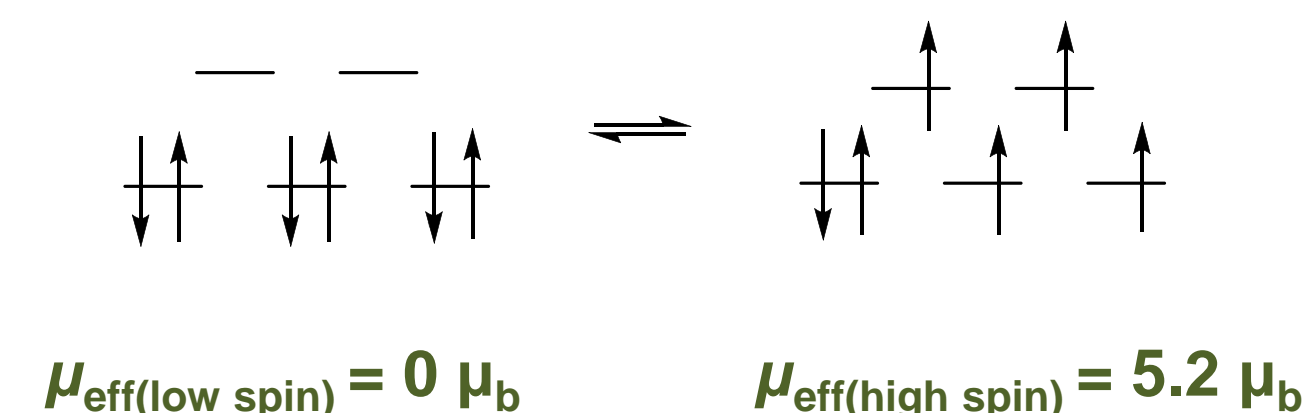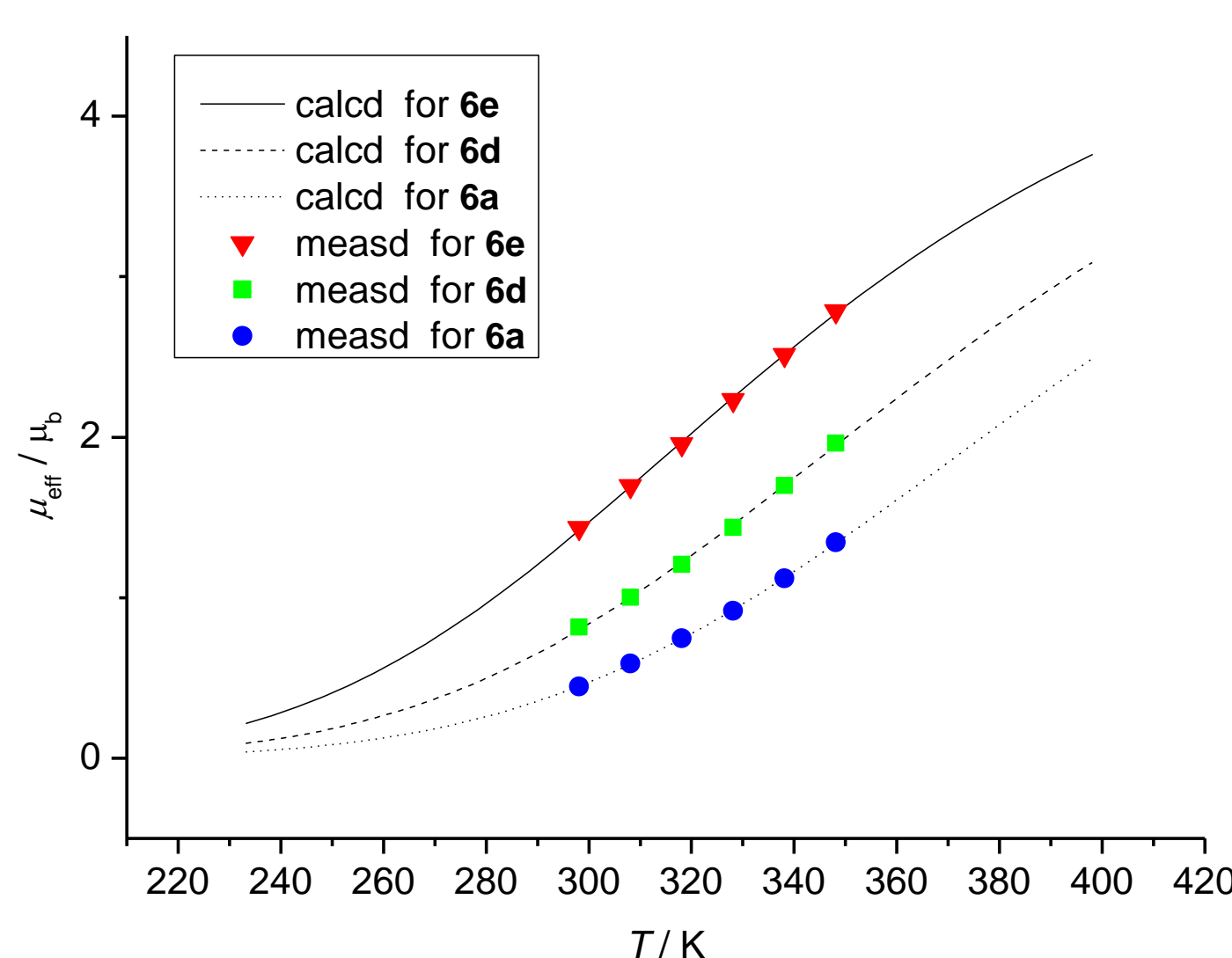
The Fe²⁺ Complexes[3]

Variation R¹

6a (R¹ = H)
$\mu_{eff(MeCN, RT)} = 0.45\ \mu_b$

6b (R¹ = OMe)
$\mu_{eff(MeCN, RT)} = 4.9\ \mu_b$
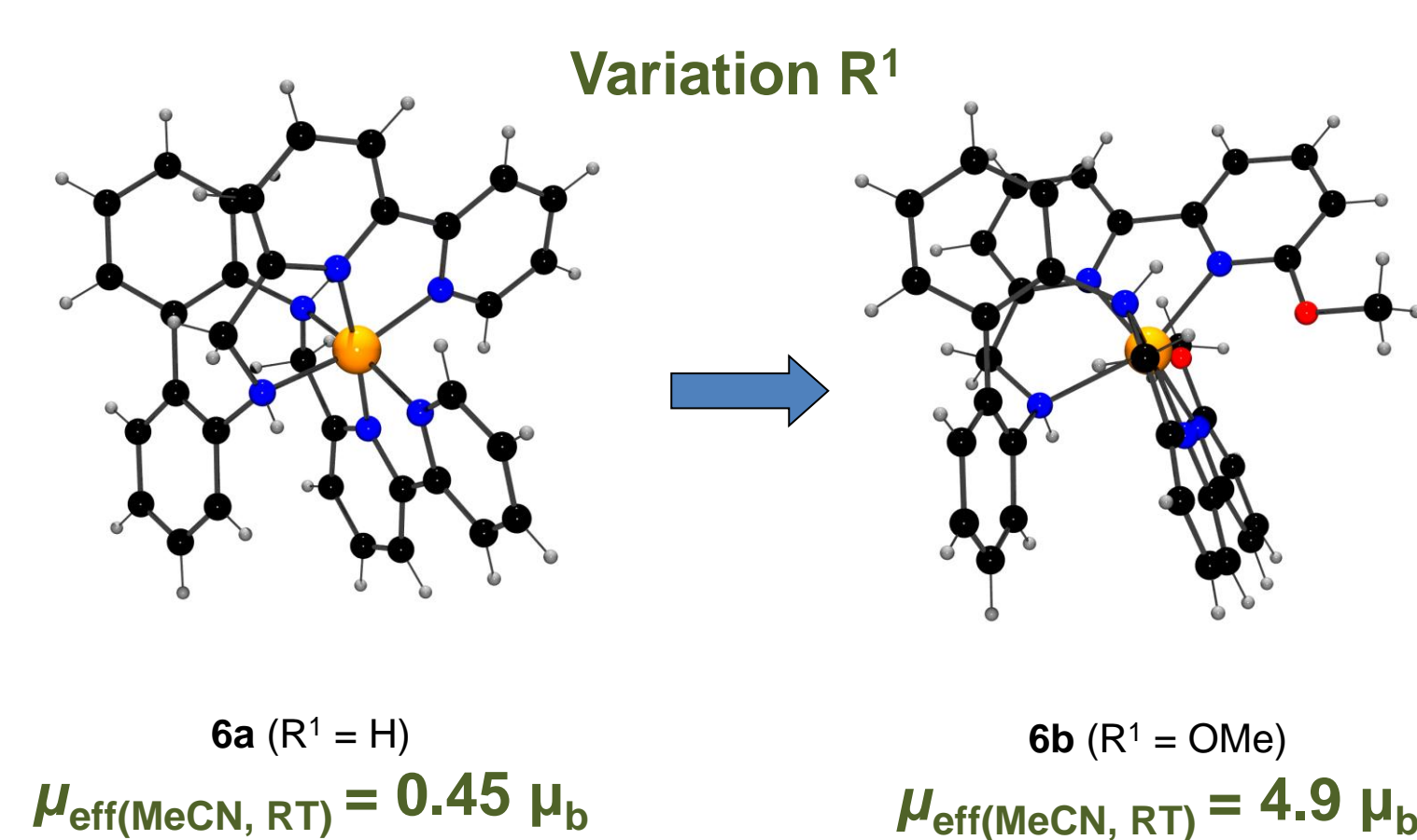
6 (R¹ @ 6'-bipy)	Fe-N (Å)$_{min/max}$ (solid @110K)	HS/LS (solid @110K)
6a (H)	1.883(4)-2.059(4)	LS
6b (OMe)	2.1067(18)-2.292(2)	HS
6c (Me)	2.1089(14)-2.2995(15)	HS

Variation R²

6a (R² = H)
$\mu_{eff(MeCN, RT)} = 0.45\ \mu_b$

6e (R² = Br)
$\mu_{eff(MeCN, RT)} = 1.43\ \mu_b$

6 (R² @ 6/6'-biphenyl)	Fe-N (Å)$_{min/max}$ (solid @110K)	HS/LS (solid @110K)
6a (H)	1.883(4)-2.059(4)	LS
6d (Me)	1.903(2)-2.071(2)	LS
6e (Br)	1.883(2)-2.068(2)	LS

$\mu_{eff(low\ spin)} = 0\ \mu_b$ $\mu_{eff(high\ spin)} = 5.2\ \mu_b$

Tuning of SCO Transition[3]

6 ($T_{1/2}$)	Δ(N-N) (Å) (solid @110K)	$\Delta(\alpha-\beta)$ (solid @110K)
6a (341 K)	3.0068(62)	2.8(10)°
6b (HS)	3.3556(29)	1.1(4)°
6c (HS)	3.3192(22)	1.6(3)°
6d (375 K)	3.0304(32)	5.0(4)°
6e (403 K)	3.0607(31)	7.8(4)°

$\alpha = \angle(1,2,3,4)$ $\beta = \angle(5,2,3,6)$

For Fe^{2+} complexes **6a** (R² = H), **6d** (R² = Me) and **6e** (R² = Br) the magnetic moments were 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 obtained about 56 J·mol⁻¹·K⁻¹, significantly different is ΔH (19.1 kJ·mol⁻¹ (**6a**), 20.6 kJ·mol⁻¹ (**6d**) and 22.5 kJ·mol⁻¹ (**6e**)). A correlation between torsion of the biphenyl bridge in solid state and $T_{1/2}$ is found. Currently we are expanding this system to a dinuclear complex 7 that could probably show a positive cooperativity of two Fe^{2+} SCO centers in solution.[4]
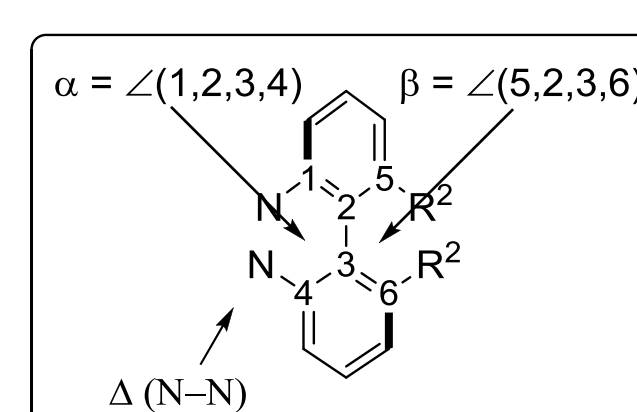
Probing Spin State by ¹H-NMR[3]
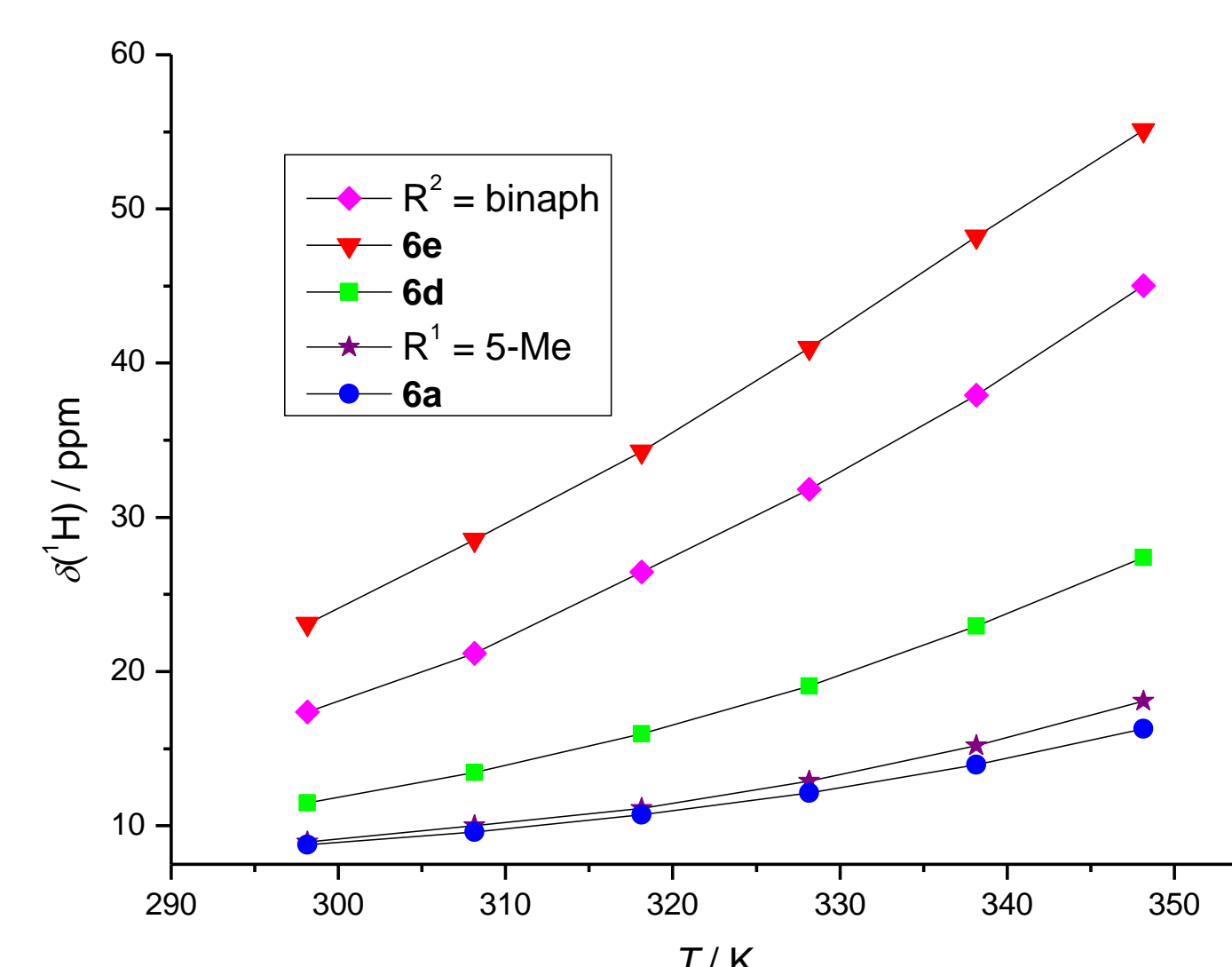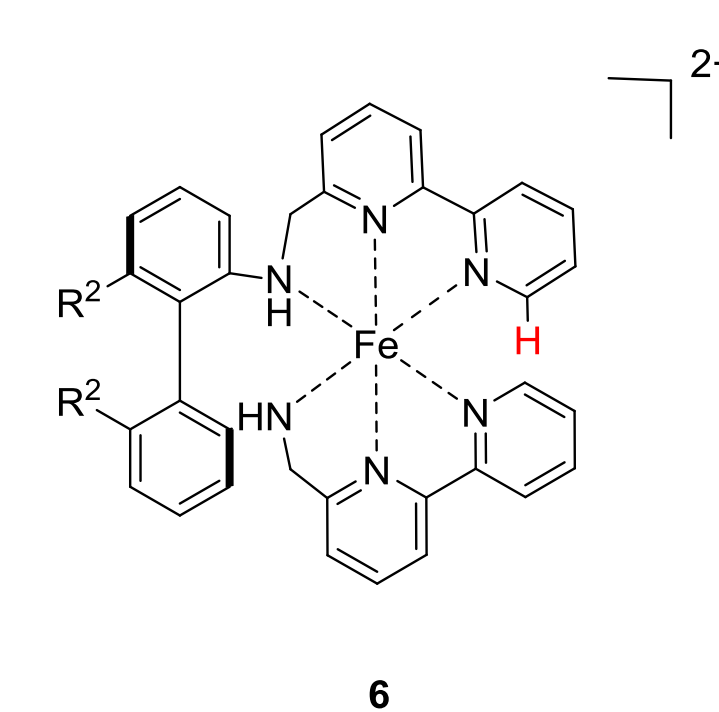
Coming soon[4]
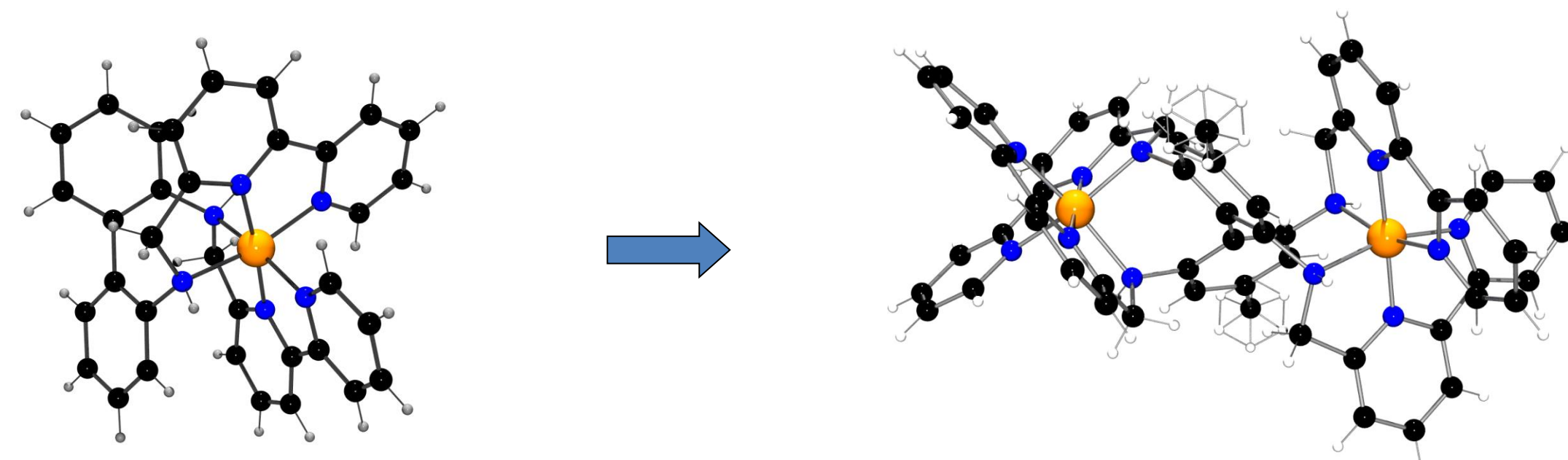
Conclusion

In summary, we have used 2,2'-bipyridin-6-carbaldehydes 3 for the synthesis of polypyridylamines 5, that are employed as ligands in Fe^{2+} spincrossover complexes 6. The used different bridges 4 allow the direct tuning of the spin transition temperature $T_{1/2}$ of the SCO complexes 6 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) E. C. Constable, G. Zhang, C. E. Housecroft, J. A. Zampese *Dalton Trans.* **2010**, 5332-5340.
[3] H. Petzold, S. Heider, *Eur. J. Inorg. Chem.* **2011**, DOI: 10.1002/ejic.201001139.
[4] S. Heider, H. Petzold, unpublished, suggested by solution-¹H-NMR.