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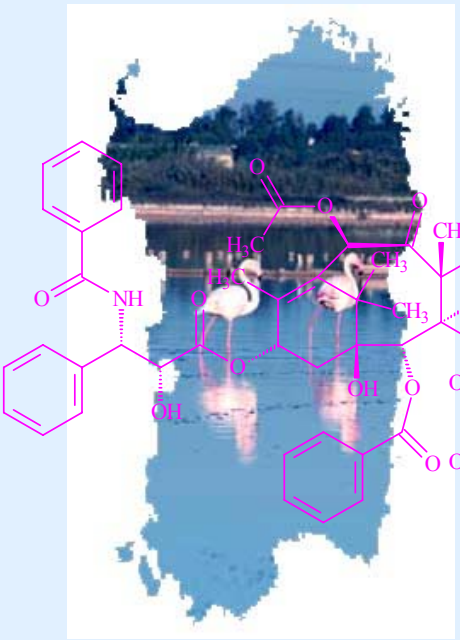
GIORNATA DI STUDIO DEDICATA ALLA CHIMICA ORGANICA DELLE MOLECOLE BIOLOGICAMENTE ATTIVE

5 Giugno 2006, Complesso Universitario di Monserrato, Cagliari



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C_1-SYMMETRY BIDENTATE FERROCENYL LIGANDS WITH PYRIDINE NITROGEN DONORS

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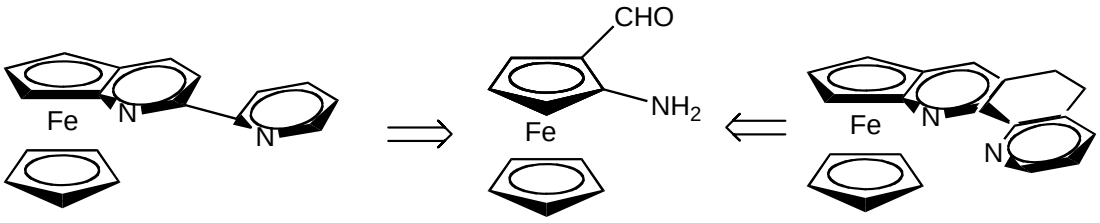
The chemistry of ferrocene is very rich and covers many areas such as material science, electrochemistry, asymmetric catalysis, etc.[1] The unique "sandwich" structure of ferrocene allows to generate a large variety of chiral compounds featuring a stereogenic plane as the sole chiral element. Among chiral ferrocenes the family of 1,2-disubstituted derivatives is by far the most numerous and a large variety of chiral ligands with different donors share this structural motif. Bidentate pyridine ligands with a stereogenic plane originating from a ferrocene scaffold are very rare and all the known examples possess C_2-symmetry.[2]
Following our long standing interest in chiral ligands with nitrogen donors recently we have devised a viable procedure for the preparation of C_1-symmetry bidentate ferrocenyl ligands with pyridine nitrogen donors.

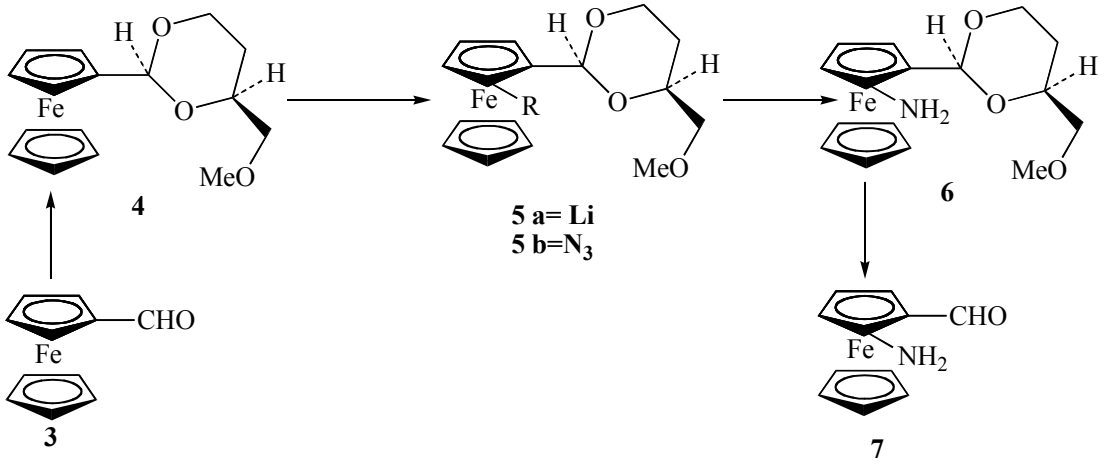


1 (S) **7 (S)** **2 (S)**

The key intermediate of this synthesis is the amino aldehyde **7** which by Friedlander-type condensation with a suitable pyridyl methyl ketone can provide a straightforward entry into C_1-symmetry bidentate ferrocenyl 2,2'-bipyridine and/or 1,10-phenanthroline ligands **1** and **2**, respectively.
For the preparation of **7** we have relied on a synthetic methodology previously adopted by Kagan for the stereoselective synthesis of 1,2-disubstituted ferrocene derivatives (Scheme 1).[3] Metallation of the enantiopure acetal **4** with *t*.butyl lithium gave the lithiated compound **5a** with complete diastereoselectivity. This was quenched with tosylazide affording the azido derivative **5b** which by reduction with sodium borohydride produced the amino acetal

6 (50% overall yield). Removal of the acetal protection with dilute HCl gave the required aminoaldehyde **7** which was stable enough as to be isolated in the solid state.

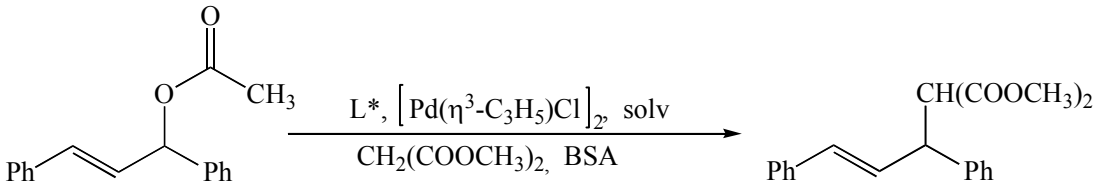
Scheme 1



Reaction of **7** with 2-acetyl pyridine or with tetrahydro quinolin-8-one in the presence of ethanolic KOH afforded the ferrocenyl substituted 2,2'-bipyridine and 5,6-dihydrophenanthroline **1** and **2**, respectively.

In the first essay, these new ligands have been screened in the Pd-catalyzed allylic alkylation of 1,3-diphenylallyl esters with dimethyl malonate (Scheme 2). The stereoselectivity of the reaction is dependent on the solvent and the acetate counterion. The best ee's have been scored in chloroform with lithium acetate as a base and thus far are not higher than 60%.

Scheme 2



References

1) *Ferrocenes*; Hayashi, T., Togni, A., Eds.; VCH: Weinheim, 1995.

2) Rios,R.; Liang, J.; Lo, M. C.; Fu , G. C. *Chem. Commun*. **2000**, 377.

3) Riant, O.; Samuel, O.; Flessner, T.; Taudien, S.; Kagan, H.B. *J.Org.Chem.* **1997**, 62, 6733-6745